REMOVAL OF REACTIVE DYES FROM AQUEOUS SOLUTION BY ADSORPTION ON COCONUT COIR ACTIVATED CARBON

RASHIDAH BT. OSMAN

CIVIL ENGINEERING
UNIVERSITI TEKNOLOGI PETRONAS
JANUARY 2009

Removal of Reactive Dyes from Aqueous Solution by Adsorption on Coconut Coir Activated Carbon

by

Rashidah bt. Othman

Dissertation submitted in partial fulfillment of
the requirements for the
Bachelor of Engineering (Hons)
(Civil Engineering)

JANUARY 2009

Universiti Teknologi PETRONAS
Bandar Seri Iskandar
31750 Tronoh
Perak Darul Ridzuan

CERTIFICATION OF APPROVAL

Removal of Reactive Dyes from Aqueous Solution by Adsorption on Coconut Coir Activated Carbon

by

Rashidah bt. Othman

A project dissertation submitted to the
Civil Engineering Programme
Universiti Teknologi PETRONAS
in partial fulfillment of the requirement for the
BACHELOR OF ENGINEERING (Hons)
(CIVIL ENGINEERING)

Approved by,

(Prof. Malay Chaudhuri)

UNIVERSITI TEKNOLOGI PETRONAS
TRONOH, PERAK
January 2009

CERTIFICATION OF ORIGINALITY

This is to certify that I am responsible for the work submitted in this project, that the original work is my own except as specified in the references and acknowledgements, and that the original work contained herein have not been undertaken or done by unspecified sources or persons.

RASHIDAH BT. OTHMAN

ABSTRACT

The removal efficiency of two highly used reactive dyes (C. I. Reactive Red 180 and C. I. Reactive Blue 19) in aqueous solution by activated carbon prepared from coconut coir was investigated. Physicochemical characteristics of the coconut coir activated carbon were measured by ash content and pH. Batch adsorption studies showed that adsorption of dyes increased with increase in contact time and carbon dose and decrease in dye concentration. Maximum decolourisation of the dyes (maximum adsorption) was observed at pH 3. The effectiveness of the coconut coir activated carbon was compared with that of a commercial charcoal activated carbon in adsorption isotherm studies where adsorption of dyes was found to fit well with the Langmuir and Freundlich models. According to the Langmuir adsorption isotherm, adsorption capacity for coconut coir activated carbon was higher for Reactive Red 180 and comparable for Reactive Blue 19 whereas adsorption energy for both dyes was higher compared to the commercial charcoal activated carbon. According to the Freundlich adsorption isotherm, the coconut coir activated carbon exhibited higher adsorption capacity for Reactive Red 180 and similar adsorption capacity for Reactive Blue 19 compared to the commercial charcoal activated carbon. The charcoal activated carbon exhibited higher adsorption energy for Reactive Red 180 and lower adsorption energy for Reactive Blue 19.

ACKNOWLEDGEMENT

I would like to thank the various people involved in making this research project a success.

First and foremost, I would like to express my sincere appreciation to Prof. Malay Chaudhuri, my research supervisor, who found time in a very busy lecture schedule for his good follow up by having regular and frequent discussions, monitor my progress and answer my questions. I am very much benefited from his professional and personal advice and I am also deeply grateful for his encouragement and patience throughout the duration of research.

Second, I would like to express my gratitude to Mr. Emad Soliman Elmolla (Post Graduate Student) for sharing his technical knowledge in answering my many questions and monitoring my laboratory works.

Third, I would like to thank Environmental Engineering Laboratory Asisstants, Encik Khairul Anwar and Cik Yusyawati for their help in handling laboratory apparatus and equipments throughout the duration of FYP. Acknowledgements also go to the Civil and Chemical Engineering Department for material support.

Fourth, I would like to thank my colleagues, Nurul Afifah binti Mohd Zaid who works with me most of the time in the laboratory, where we supporting each other and defeating all difficulties together.

Finally, I would like to express my sincerest appreciation to my parents, colleagues and friends for helping me on making this research a success. Thank you for the personal advice, everlasting support and encouragement.

TABLE OF CONTENTS

LIST OF FIGURES

LIST OF TABLES

LIST OF ABBREVIATION AND NOMENCLATURES

ABBREVIATION

C. I.	Colour Index
FYP	Final Year Project
GAC	Granular Activated Carbon
HCS	Hazard Communication Standard
MSDS	Material Safety Data Sheets
OSHA	Occupational Safety and Health Administration
PAC	Powdered Activated Carbon
PPE	Personal Protective Equipment
SEM	Scanning Electron Micrograph
UTP	Universiti Teknologi Petronas
VPSEM	Variable Pressure Scanning Electron Micrograph

NOMENCLATURES

HCl	Hydrochloric Acid
H_2SO_4	Sulfuric Acid
NaOH	Sodium Hydroxide

CHAPTER 1

INTRODUCTION

1.1 BACKGROUND OF STUDY

Dyes are chemicals which on binding with a material to produce colour to the material, such as fabric. Dyes that form a covalent bond with the substrate during the dyeing process are known as reactive dyes. There is a rapid growth rate in the used of reactive dyes due to the increasing use of cellulosic fibres and the technical and economic limitations of other dyes used for these fibres (Allen and Koumanova, 2005). Coloured dye effluent arises as a direct result of the dye production and it is estimated that 10–15% of the dye is lost in the effluent during the dyeing process (Garg et al., 2003; Young and Yu, 1997).

Adsorption techniques for wastewater treatment have become more popular in recent years owing to their efficiency in the removal of pollutants too stable for biological methods, hence producing high quality water (Allen and Koumanova, 2005). Adsorption has been found to be superior to other techniques for wastewater treatment in terms of initial cost, simplicity of design, ease of operation and insensivity to toxic substances. McKay (1982) specifies the main adsorbent that has been widely used in industry as activated carbon which comes in the form of granular (GAC) or powder (PAC).

1.2 PROBLEM STATEMENT

Carr (1995) indicates 40% of the colour is discharged in the effluent from reactive dyeing operation resulting in a highly coloured effluent. An additional problem is the reactive dyes in both ordinary and hydrolysed forms are not easily biodegradable, hence even after extensive treatment; colour may still remain in the effluent. The conventional processes such as coagulation, flocculation and biological methods adopted for decolourising effluent containing reactive dyes are no longer effective to achieve an adequate colour removal.

Strickland and Perkins (1995) testified the greatest environmental concern with dyes are their absorption and reflection of sunlight entering the water which interferes with the growth of bacteria to levels insufficient to biologically degrade impurities in the water. Colour in effluents can cause problems in several ways. Dyes can have acute and chronic effects on exposed organisms depending on the exposure time and dye concentration. Dyes are inherently highly visible, meaning that the concentrations as low as 0.005 ppm capture the attention of both the public and the authorities (Pierce, 1994). Dyes also absorb and reflect sunlight entering water and so can interfere with the growth of bacteria and hinder photosynthesis in aquatic plants (Slokar and Marechal, 1998).

Kharaisheh et al. (2002) reported that reactive dye is known to have low absorbability on a wide range of adsorbents. Reactive dye wastewater has limited biodegradability in an aerobic environment. Many reactive azo dyes, constituting the largest dye groups decompose to potential carcinogenic aromatic amines under anaerobic conditions (Lazearidis et al., 2003; Netpradit et al., 2003). Adsorption has proved to be more versatile and efficient compared to conventional physico-chemical methods of dye removal (Senthilkumar et al., 2006). Garg et al. (2004) agree adsorption methods using activated carbon have been invariably successful to decolourise dye effluents due to its large surface area, microporous structure, high adsorption capacity, etc. However, this application is limited by the high cost of adsorbents.

1.3 OBJECTIVE AND SCOPE OF STUDY

The main objectives of this study are:

1) To investigate the removal of two highly used reactive dyes in aqueous solution by adsorption on coconut coir activated carbon
    i) C. I. Reactive Red 180
    ii) C. I. Reactive Blue 19
2) To compare the effectiveness of the prepared coconut coir activated carbon with a commercial charcoal activated carbon

Scope of study of this research is primarily to investigate adsorptive removal of two reactive dyes in aqueous solution by coconut coir activated carbon in batch studies where effect of initial concentration, contact time, pH and carbon dose will be observed. Optimum condition obtained from batch studies will then be used in adsorption isotherm studies. By plotting Langmuir and Freundlich adsorption isotherms, the effectiveness of the prepared coconut coir activated carbon will be compared with a commercial charcoal activated carbon.

1.4 RELEVANCY OF THE PROJECT

In most countries including Malaysia, coconut coir is one of the organic material produce from agricultural industries. It is always treated as a waste objects that can cause disposal problem because of its resistance to biodegradation. Since coconut coir is rich in lignocellulosic content, a further attempt is taken to investigate the efficiency of this waste material to remove reactive dyes in aqueous solution such as effluent from textile industry. Despite the fact that commercial activated carbon is already available in the market, it is however limited to high cost in production and regeneration of spent carbon, which is not suitable to be used in a developing countries. Therefore, activated carbon prepared by coconut coir is very suitable to replace the commercial activated carbon as it is economical, reliable and high in quality.

1.5 FEASIBILITY OF THE PROJECT

Preparation of coconut coir activated carbon is relatively difficult and requires extra effort and attention, precise measurement of materials and consistency in doing the laboratory works. To obtain a good and high quality of coconut coir activated carbon, all procedures must be done carefully and accurately. Small mistakes in doing laboratory testing may render the efficiency of coconut coir activated carbon. The experimental works need to be done in stages, until satisfactory result is obtained before proceeding to the next stages. The coconut coir activated carbon is prepared from Part 1 of the FYP and will continue until the amount of carbon is sufficient to run all the tests and experiments. Only after the quality of prepared coconut coir activated carbon is found to be favorable, batch studies and adsorption isotherm studies will be preceded.

The two reactive dyes used in this study were collected from TCB Batik & Songket Sdn. Bhd. in Kuala Terengganu, Terengganu while the commercial charcoal activated carbon was obtained from UTP Chemical Engineering Department Laboratory, supplied by Benua Sains Sdn. Bhd., Puchong, Selangor.

CHAPTER 2

LITERATURE REVIEW

2.1 ADSORPTION

Dyes laden wastewater is usually treated by physical or chemical processes. These include flocculation, electro-floatation, precipitation, electro-kinetic coagulation, ion exchange, membrane filtration, electrochemical destruction, irradiation, ozonation and Katox treatment method involving the use of activated carbon and air mixtures (Banat, 1996). However, these processes are expensive and sometimes ineffective to treat the wide range of dye wastewater. For that reason, adsorption technique for wastewater treatment has become more popular in recent years due to the effectiveness in removing pollutants and economical.

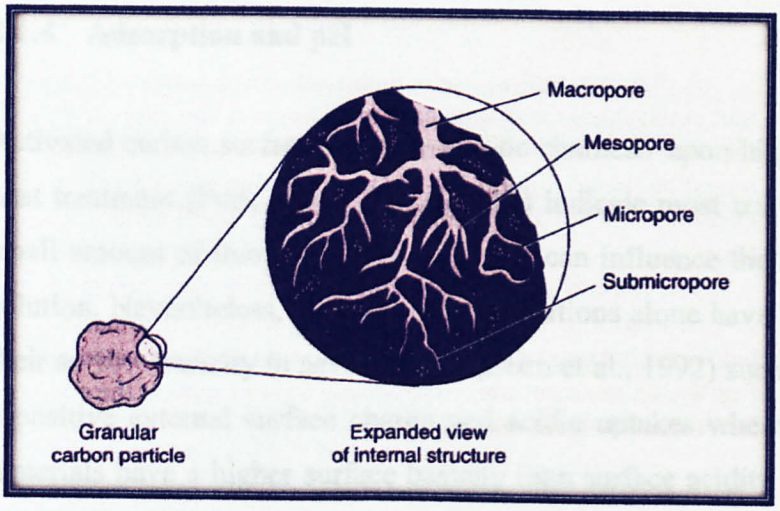
2.1.1 Adsorption Theories and Principles

As noted in Wastewater Engineering – Treatment and Reuse by Metcalf & Eddy, Inc. (1994), adsorption is the process of accumulating substances that are in solution on a suitable interface. Adsorption is a mass transfer operation in that a constituent in the liquid phase is transferred to the solid phase. The adsorbate is the substance that is being removed from the liquid phase at the interface. The adsorbent is the solid, liquid or gas phase onto which the adsorbate accumulates. Decolourisation is a result of two mechanisms – adsorption and ion exchange (Slokar and Le Marechal, 1998), and is influenced by many factors including dye/sorbent interaction, sorbent surface area, particle size, temperature, pH and contact time. Ruthven (1984) reveal that physical adsorption occurs when weak interparticle bonds exist between the adsorbate and adsorbent. Examples of such bonds are van der Waals, hydrogen and dipole-dipole. In the majority of cases, physical adsorption is easily reversible.

Chemical adsorption occurs when strong interparticle bonds are present between the adsorbate and adsorbent due to an exchange of electrons. Examples of such bonds are covalent and ionic bonds. Chemisorptions are deemed to be irreversible in the majority of cases (Ruthven, 1984). Suzuki (1997) covers the role of adsorption in water environmental processes and also covers the development of newer adsorbents to modernize the treatment systems and the role modeling of the findings plays in their development. Most adsorbents are highly porous materials. As the pores are generally small, the internal surface area is orders of magnitude greater than the external area. Separation occurs because differences in molecular mass, shape or polarity causing some molecules to be held more strongly on the surface than others or because the pores are too small to admit the large molecules (Suzuki, 1990).

2.1.2 Adsorption by Activated Carbon

Metcalf & Eddy Inc. (1994) indicates that adsorption process takes place in three major steps, namely macrotransport, microtransport and sorption. Macrotransport consists the movement of adsorbate by advection and diffusion through the water to the liquid or solid phase. Microtransport involves the diffusion of the organic material through the macropore system of the solid adsorbent to the adsorption sites in the micropores and the solid adsorbent. Graphical diagram of activated carbon can be observed in Figure 2.1.



(Adopted from Wastewater Engineering - Treatment and Reuse by Metcalf & Eddy Inc., 1994)

Figure 2.1 Macropore, mesopore, micropore and submicropore adsorption sites on activated carbon.

Adsorption also may occur on the surface of the solid adsorbent and in the macropores and mesopores, the surface area of these parts of most solid adsorbents is relatively small compared with the surface area of the micropores. Hence, the amount of material adsorbed is usually considered as negligible. (Metcalf and Eddy Inc., 1994)

2.1.3 Adsorption of Reactive Dyes

Al-Degs et al. (2000) investigated the effect of activated carbon surface chemistry on the adsorption of three reactive dyes in aqueous solution. In this work, it is confirmed the adsorption capacity for reactive dyes increased with a decrease in the activated carbon particle manner. Al-Degs et al. (2000) also indicates that the adsorption capacity for Remazol dyes on granular activated carbon Filtrasorb 400 is reduced upon mixing in multi-component solutions. Allen et al. (1988) considered the competitive adsorption of three basic dyes and the results showed that the adsorption capacity of an individual dye decreased in the presence of a second or a third dye. The reduced capacities can be attributed to a number of factors including interaction between dyes in solution, change of the adsorbent surface charge due to adsorption, competitive adsorption between the dyes for active sites on the activated carbon surface where displacement effects replace the other dyes from the adsorption sites.

2.1.4 Adsorption and pH

Activated carbon surfaces acquire a basic character upon high temperature (>973 K) heat treatment (Puri, 1994). Parks (1965) indicate most activated carbons contain a small amount of inorganic impurities that can influence their acid/base responses in solution. Nevertheless, the pure organic portions alone have been shown to manifest their surface basicity in several ways (Leon et al., 1992) such as a pH value above 7, a positive external surface charge and acidic uptakes where most activated carbon materials have a higher surface basicity than surface acidity (Moreno-Castilla et al., 1997). Undoubtedly, the pH value of the dye solution plays an important role in the whole adsorption process and particularly on the adsorption capacity.

2.1.5 Adsorption Isotherm

Primarily purpose of adsorption is accumulating substances that are in solution on a suitable interface. Two type of activated carbon in the form of granular (GAC) and powdered (PAC) are commonly used to remove selected constituents from wastewater. Metcalf & Eddy Inc. (1994) described that adsorption isotherm is the accumulation of material, which is used to define the mass of material adsorbed per unit mass of adsorbing material.

2.1.5.1 Langmuir Isotherm

Langmuir isotherm also can be used instead of Freundlich isotherm. From rational considerations, the Langmuir isotherm is described as:

$$\frac{x}{m} = \frac{abC_e}{1 + C_e} \tag{2-1}$$

where $\frac{x}{m}$ = mass of the adsorbate adsorbed per unit mass of adsorbent, mg adsorbent per g of activated carbon

a, b = empirical constant (a is adsorption capacity and b is adsorption energy)

C_e = equilibrium concentration of adsorbate in solution after adsorption, mg/L

The Langmuir adsorption isotherm is developed by assuming that a fixed number of accessible sites are available on the adsorbent surface, all of which have the same energy, and adsorption is reversible. When the rate of adsorption of molecules onto the surface is the same as the rate of desorption of molecules from the surface, equilibrium is finally reached.

In the Langmuir isotherm, constant can be determined by plotting $C_e/(x/m)$ versus C_e and making used the previous equation rewritten as shown in Equation 2-2.

$$\frac{C_e}{(x/m)} = \frac{1}{ab} + \frac{1}{a}C_e \tag{2-2}$$

2.1.5.2 *Freundlich Isotherm*

A widely applied adsorption isotherm is the Freundlich isotherm. Derivation of empirical considerations in the Freundlich isotherm is identified as below:

$$q_e = \frac{x}{m} = K_f C_e{}^{1/n} \tag{2-3}$$

Where q_e = mass of material adsorbed (x) per unit mass of adsorbent (m) at equilibrium
K_f = Freundlich capacity factor
C_e = equilibrium concentration of adsorbate in liquid phase after adsorption, mg/L
$1/n$ = Freundlich intensity parameter

According to Weber (1972), the Freundlich equation is basically empirical but is often useful as a means for data description. Data are usually fitted to the logarithmic form of the equation:

$$\log q_e = log K_f + \frac{1}{n} \log C_e \tag{2-4}$$

where the intercept is roughly an indicator of adsorption capacity and the slope 1/n, of adsorption intensity.

Weber (1972) also indicates that the Freundlich equation generally agrees quite well with the Langmuir equation and experimental data over moderate ranges of concentration. However, Freundlich equation does not reduce to a linear adsorption expression at very low or high concentrations unlike Langmuir equation since *n* must reach some limit when the surface is fully covered.

2.2 ACTIVATED CARBON

Activated carbon is usually manufactured by wide variety of raw materials such as coal, wood, peat and petroleum coke. The predominant qualification for the materials to be activated carbon is having high percentage of carbon content. Chemical and thermal processes are also involved in the process of converting the raw material into finished adsorbent.

Activated carbons may come in different physical forms depending on their application. Granular (GAC) forms are normally used in adsorption columns and powder (PAC) forms for use in batch adsorption followed by filtration. The characteristics of granular and powdered activated carbon are summarized in Table 2.1.

Table 2.1 Comparison of granular and powdered activated carbon

Parameter	Unit	Type of activated carbon	
		GAC	PAC
Total surface area	m^2/g	700–1300	800–1800
Bulk density	kg/m^3	400–500	360–740
Particle density, wetted in water	kg/L	1.0–1.5	1.3–1.4
Particle size range	mm(m)	0.1–2.36	(5–50)
Effective size	mm	0.6–0.9	na
Uniformity coefficient	UC	≤1.9	na
Mean pore radius		16–30	20–40
Iodine number		600–1100	800–1200
Abrasion number	minimum	75–85	70–80
Ash	%	≤8	≤6
Moisture as packed	%	2–8	3–10

* Specific values will depend on the source material used for the production of the activated carbon.

Source: Wastewater Engineering - Treatment and Reuse by Metcalf & Eddy Inc., 1994

The activated carbon has an incredibly large surface area and a network of submicroscopic pores where adsorption takes place. The walls of the pores provide the surface layer molecules essential for adsorption process. Amazingly, one pound of carbon provides a surface area equivalent to six football fields.

Generally, PAC is preferred over GAC in liquid phase batch application because of their high adsorption capacity. However, the dusty nature of PACs poses handling problems and makes regeneration ineffective. In order to use this material for continuous treatment of wastewater, Santhy and Selvapathy (2006) converted the powdered to granular form by agglomerating with polyvinyl acetate emulsion. Typically, the PAC has a diameter of less than 0.074 mm (200 sieve), and a GAC has a diameter greater than 0.1 mm (~140sieve).

Activated carbon works to remove contaminants from water by primary means of physical adsorption. Carbon's highly porous nature provides large surface area for the adsorbates (contaminants) to collect. In other words, all molecules exert attractive forces during physical adsorption, especially molecules located at the surface of a solid (pore walls of carbon) and these surface molecules consequently seek other molecules to adhere to.

Adsorption from solution occurs as a result of differences in carbon pores with adsorbate concentration in the solution. During adsorption process, the adsorbate migrates from the solution through the pore channels and reaches the area where the strongest forces are available. For instance, in removal of dyes, color from the dye solution will migrates to the pore opening of activated carbon.

2.2.1 Charcoal Activated Carbon

Charcoal activated carbon is produced from wood as it contains a large amount of water and volatile organic compounds such as sap. Sap is considered as volatile because it is combustible and evaporates when heated. Carbon and ash also contribute to the make up of a piece of wood; where ash is made up of the non-combustible elements in the wood such as calcium, magnesium and potassium.

During flaming process of woods by fire, the smoke being produced is actually the volatile organic compounds evaporating into the atmosphere. In order to produce charcoal, the wood must be heated without the presence of oxygen. Therefore, the wood will be burned at very high temperatures in clay or steel boxes.

The charcoal becomes activated after it is treated with oxygen to open up pores. When activated, it has a very fine particle size and a very large surface area that has the ability to absorb or have other substances attach to it. Opening up these tiny pores between atoms expands the surface area of the carbon enormously. Carbon is a naturally absorbent element, and it is able to absorb a wide variety of harmful chemicals. The large surface area of activated charcoal allows it to absorb and trap millions of chemicals at its countless bonding sites.

Figure 2.2 Charcoal activated carbon

2.3 REACTIVE DYE

Reactive dye is a class of highly coloured organic substances, which attach to the substrates by chemical reaction and forms a covalent bond between the molecule of dye and the fibre. The dyestuff therefore becomes part of the fibre and much less likely to be removed by washing.

The reactive dyes are originally designed for cellulose fibres but also can be used for polyamide, cotton, linen, wool and nylon. In theory, when the dyes are applied to a fibre in a weakly alkaline dyebath, the reactive group will form a chemical bond with the fibre. Thus, the most important characteristics of reactive dyes are the formation of covalent bond with the substrate to be coloured.

Today, reactive dyeing in textile industries is currently the most widespread process in the world. Reactive dyes are superior compared to all other dyes because it binds chemically to the textile fibres, hence significantly improving the product's colour stability and wash ability.

2.4 COCONUT COIR

Coconut coir is a light fluffy biomaterial, which is generated in the separation process of the fibre from coconut husk. Statistic taken from Malaysian's Ministry of Agriculture & Agro-Based Industry and Ministry of Plantation Industries & Commodities (Table 2.2) indicates growth in the land use for coconut farm increase from 159,000 to 180,000 hectares in the year 2000 to 2010 (Wong, 2006), hence causing disposal problem to the environment as abundant of coir is produced. Raw coir pith consists of 35.0% cellulose, 25.2% lignin, 7.5% pentosans, 1.8% fats and resins, 8.7% ash contents, 11.9% moisture content and 10.6% other substances (Dan, 1993).

Table 2.2 Agriculture Land Use in Malaysia, 2000-2010

Crop	Hectares ('000)			Average Annual Growth Rate (%)		
				8th Malaysian Plan		9th Malaysian Plan
	2000	2005	2010	Target	Achieved	
Oil Palm	3,377	4,049	4,555	3.2	3.7	2.4
Rubber	1,431	1,250	1,179	-2.7	-2.7	-1.2
Padi	478	452	450	-0.5	-1.1	-0.1
Fruits	304	330	375	5.1	1.7	2.6
Coconut	159	180	180	-0.6	2.5	0.0
Cocoa	76	33	45	-2.4	-15.2	6.2
Vegetables	40	64	86	4.2	9.9	6.1
Tobacco	15	11	7	2.5	-6.0	-7.4
Pepper	13	13	14	2.1	0.0	0.6
Total	**5,893**	**6,383**	**6,891**	**1.5**	**1.6**	**1.5**

Source: Ministry of Agriculture and Agro-Based Industry and Ministry of Plantation Industries and Commodities

Figure 2.3 Raw coconut coir

Close view of coir fiber observed using Scanning Electron Micrograph (SEM) under 100× and 500× magnifications are as followed:

Figure 2.4 Coconut coir fibers under 100× and 500× magnifications

From both photographs, it is viewed that the fiber surface of coconut coir is covered with protrusions and small voids. Since coconut coir rich in lignocellulosic content, effective solution are taken by Namasivayam et al. (2001) to prepare coconut coir pith activated carbon, which is successful for the removal of dyes. A further attempt of the feasibility applying activated carbon from coconut coir towards the removal of reactive dyes from aqueous solution and industrial effluents is approached in this research.

CHAPTER 3

MATERIALS AND METHODS

3.1 REACTIVE DYE

3.1.1 C. I. Reactive Red 180

Reactive Red 180 has advantage of high exhaustion, high fixation, high alkali stability, very good leveling property, excellent all around fastness properties like light, washing, perspiration and rubbing chlorine peroxide bleach. Other properties of this dye can be referred in Table 3.1.

Table 3.1 Properties of C.I. Reactive Red 180

Properties	Descriptions
C. I. Name	Reactive Red 180
C. I. Number	-
CAS Number	98114-32-0
Product Code	Remazol Red F-3B
Other Names	Brilliant Rot F3B
Chemical Structure	[5-(benzoylamino)-4-hydroxy-3-((1-sulfo-6-((2-(sulfooxy)ethyl)sulfonyl)-2-naphthalenyl)azo)-2,7-naphthalenedisulfonic acid, tetrasodium salt]
Supplier	TCB Batik & Songket Sdn. Bhd., Kuala Terengganu, Terengganu

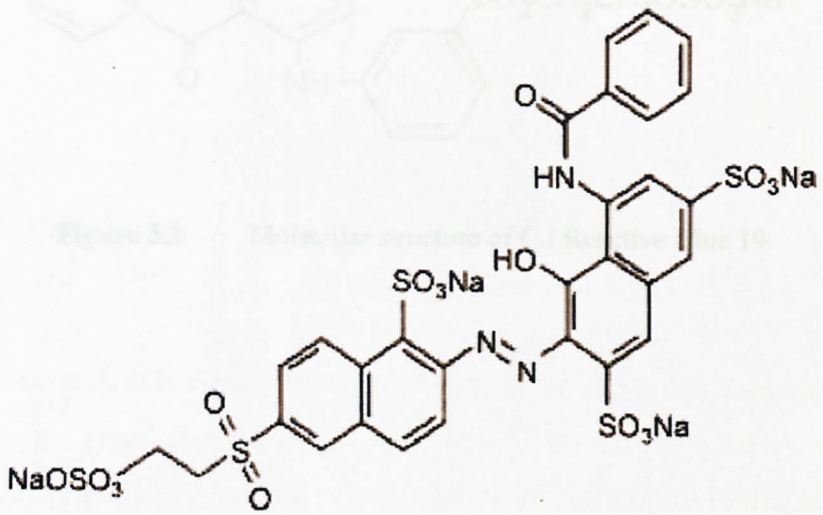


Figure 3.1 Molecular structure of C.I Reactive Red 180

3.1.2 C. I. Reactive Blue 19

C. I. Reactive Blue 19 is a vinyl sulphone dyes, also known as Remazol® dyes widely used for dyeing and printing of cellulosic fibres for its very good fastness properties. This dye has good solubility even in presence of alkali and possesses less affinity, hence very good leveling property and suitable for resist and discharge printing very much effectively. Other properties of the dye are noted in the following Table:

Table 3.2 Properties of C.I. Reactive Blue 19

Properties	Descriptions
C. I. Name	Reactive Blue 19
C. I. Number	61200
CAS Number	2580-78-1
Product Code	Remazol Blue (Special)
Other Names	Brilliant Blue R
Chemical Structure	[2-anthracene-sulfonic acid, 1-amino-9, 10-dihydro-9, 10-dioxo-4-((3-((2-(sulfooxy) ethyl)sulfonyl)phenyl)amino)-, disodium salt]
Supplier	TCB Batik & Songket Sdn. Bhd., Kuala Terengganu, Terengganu

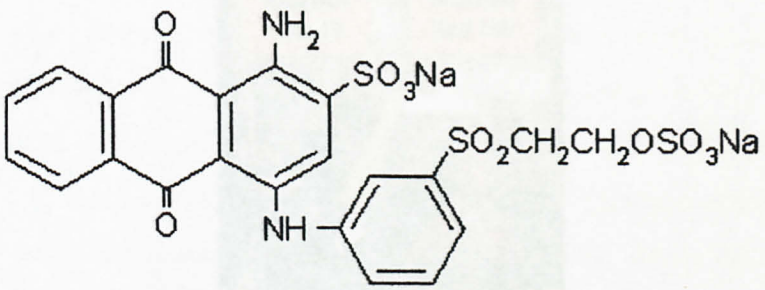


Figure 3.2 Molecular structure of C.I Reactive Blue 19

3.2 DYE CONCENTRATION & ABSORBANCE

Two reactive dyes namely Reactive Red 180 and Reactive Blue 19 are used in this study. The dyes are collected from TCB Batik & Songket Sdn. Bhd., in Kuala Terengganu, Terengganu. Dye concentration was determined by finding the maximum wavelength of absorbance for dye in concentration of 20 mg/L. To obtain 20 mg/L dye concentration, first, one stock solution of 100 mg/L was composed by adding 0.1000 g of reactive dye in powder form into 1 Liter of distilled water. It is a necessity to ensure that the reactive dye was exactly 0.1000 g in amount using digital analytical balance to avoid any errors later in adsorption studies.

Then, the stock solution of 100 mg/L was diluted by mixing 100 mL of the stock solution with 400 mL of distilled water in a 500 mL volumetric flask to obtain 20 mg/L dye concentration. After that, the 20 mg/L dye concentration was analyzed spectrophotometrically to obtain dye absorbance and wavelength by setting manually the numerous values of wavelength. Distilled water was used as a blank sample for each dye absorbance determination of new wavelength. At the end of the test, wavelength at highest dye absorbance was chosen for further studies used.

Figure 3.3 100 mg/L stock solution

By using wavelength at highest dye absorbance of 20 mg/L dye concentration, dye absorbances for other concentrations were measured. Standard curve was plotted from the results obtained and can be referred in further studies. Dilution factor for other dye concentrations based on the 100 mg/L stock solution can be determined in Appendix 1.

3.3 COCONUT COIR ACTIVATED CARBON

Preparation of activated carbon was quite difficult, requires extra effort and attention, precise measurement of materials and consistency in doing the laboratory works. By referring to Santhy and Selvapathy (2006), the activated carbon was generated using coconut coir instead of coconut coir pith. The difference between the coconut coir and coconut coir pith was the composition of the coir. The coir pith was obtained after separation of the fiber from the coconut husk while the coconut coir that used in this research includes both fiber and husk from the coconut fruit.

Preparation of activated carbon started by grinding the raw coconut coir using electric mixer and washing with distilled water to avoid contamination with dirt and dust. The coir was dried in an air oven maintained at 105 ± 5 °C until all the moisture evaporated. Then, 50 g of the dried coconut coir was mixed with 50 mL of concentrated sulfuric acid and this combination were kept in an air oven maintained at 105 ± 5 °C for 24 hours. During this process, the dried coconut coir was ensured fully in contact with the concentrated sulfuric acid, hence resulting the char becomes black in colour after 24 hours.

Next, the resulted char was washed with water followed by a 2% solution of sodium bicarbonate until effervescence had ceased and kept the char in a 2% solution of sodium bicarbonate overnight (for about 12 hours). After that, the char was separated and washed with water until free from bicarbonate and dried. The char was then activated at a temperature of 900 °C in an atmosphere of Nitrogen for 30 minutes by using Fixed Bed Activation Unit (see Figure 3.5). The activated material was repeatedly washed with water and soaked in 10% hydrochloric acid to remove calcium oxide. The acid washed material was repeatedly washed with water once again to remove the free acid and then dried in an air oven maintained at 105 ± 5 °C. Finally, the resulted material was sieved and particle sizes within the range of 0.2–0.5 mm (400–500 μm) are placed in an airtight container for use in further studies.

The flow chart of the processes involve in preparing coconut activated carbon is given on Figure 3.4 and photographs pertaining the methods are attached in Appendix 2.

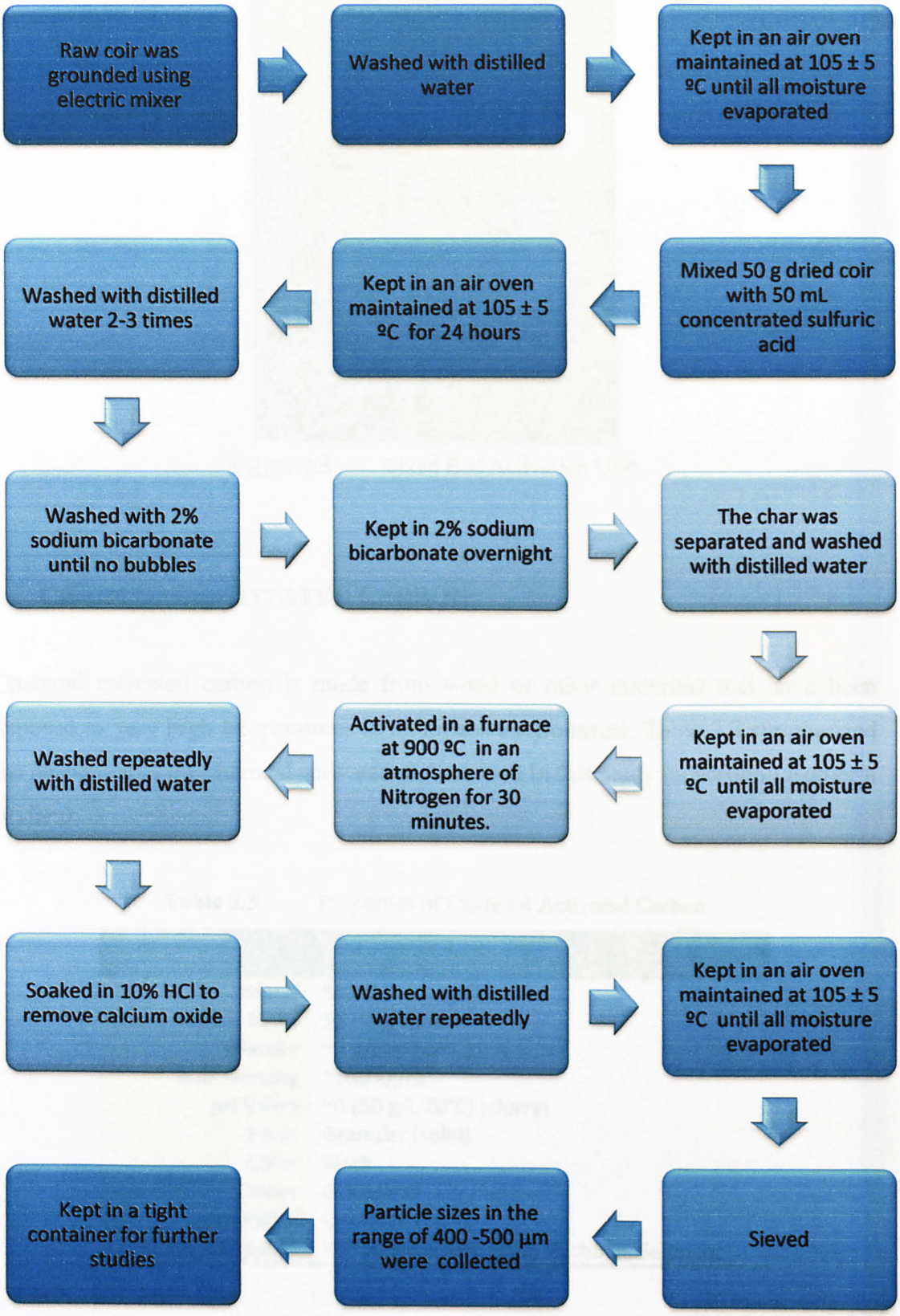


Figure 3.4 Preparation of coconut coir activated carbon

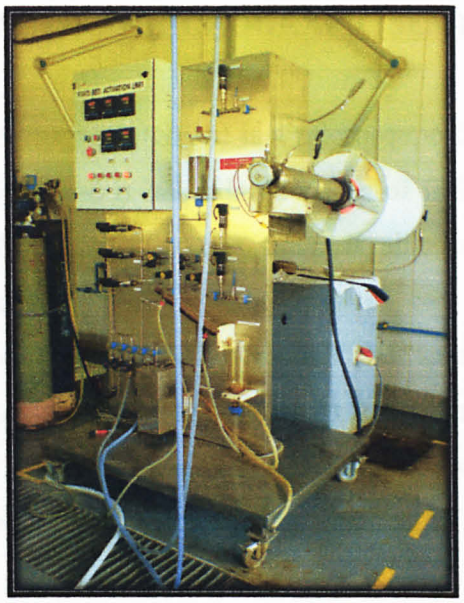


Figure 3.5 Fixed Bed Activation Unit

3.4 CHARCOAL ACTIVATED CARBON

Charcoal activated carbon is made from wood or other materials that have been exposed to very high temperatures in an airless environment. Table 3.3 summarized the properties of the charcoal activated carbon used in this study (adsorption isotherm studies).

Table 3.3 Properties of Charcoal Activated Carbon

Properties	Descriptions
Brand	Merck
Molar Mass	12.01 g/mol
Density	~2 g/cm^3 (20°C)
Bulk Density	~400 kg/m^3
pH Value	~6 (50 g/L 20°C) (slurry)
Form	Granular (solid)
Color	Black
Odour	Odourless
Solubility	Insoluble (20°C)
Supplier	Benua Sains Sdn. Bhd., Puchong, Selangor

3.5 SCANNING ELECTRON MICROGRAPH (SEM)

The Scanning Electron Micrograph (SEM) is a microscope that uses electrons rather than light to form an image and it has a large depth of field, which allows a large amount of sample to be in focus at one time. It also produce images of high resolution, which means that closely spaced features can be examined at a high magnification. Since most SEMs only require the sample to be conductive, preparation of the samples is relatively easy. In UTP Laboratory, the SEMs of coconut coir activated carbon and charcoal activated carbon are determined from LEO 1430 VPSEM (Variable Pressure Scanning Electron Micrograph).

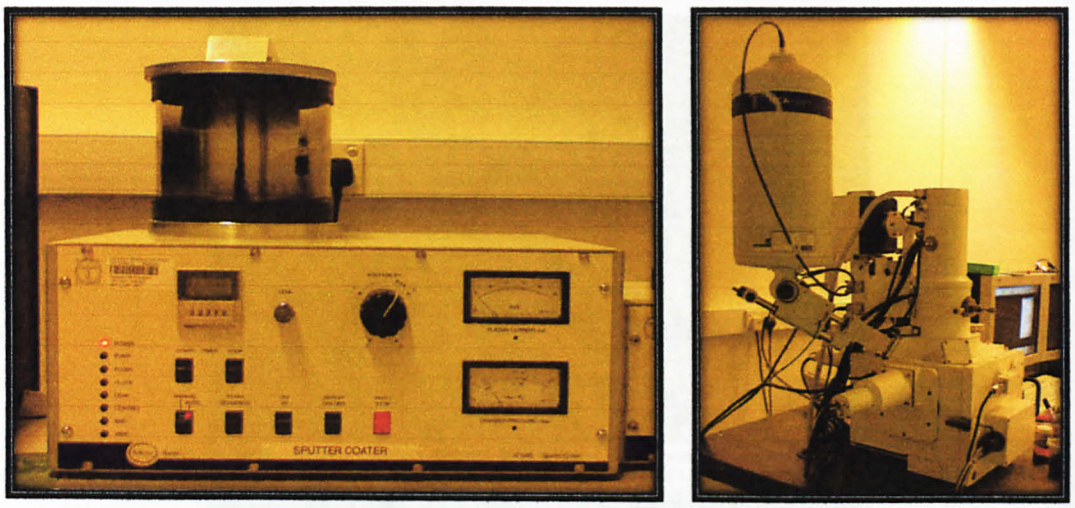


Figure 3.6 LEO 1430 Variable Pressure Scanning Electron Micrograph (VPSEM)

3.5.1 SEMs of Coconut Coir Activated Carbon

The photographs of coconut coir activated carbon in three different magnifications were shown in the following figure where the void, porosity and surface area of the carbon can be observed clearly.

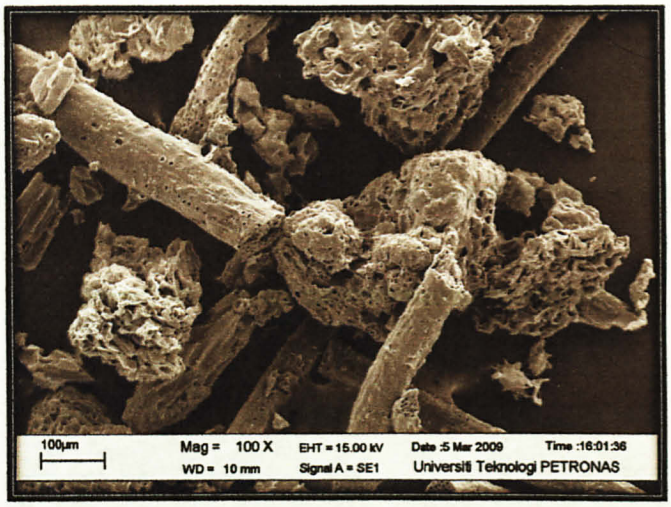


Figure 3.7 Coconut coir activated carbon under 100× magnifications

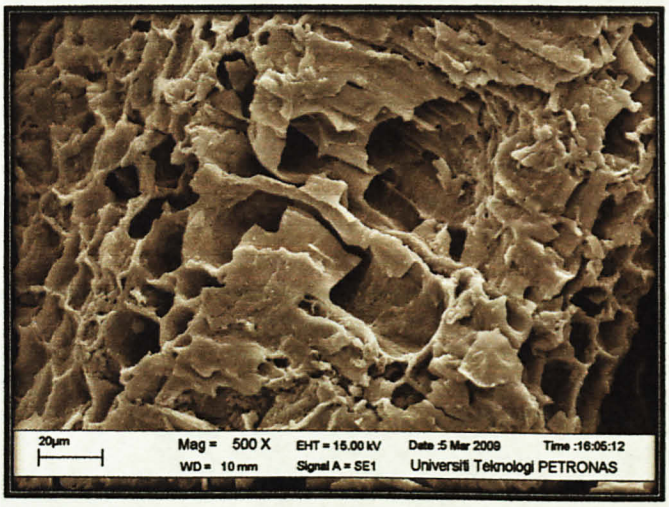


Figure 3.8 Coconut coir activated carbon under 500× magnifications

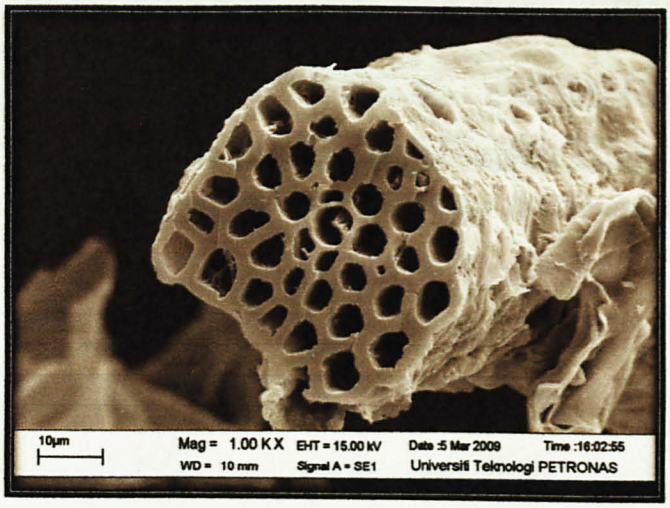


Figure 3.9 Coconut coir activated carbon under 1000× magnifications

3.5.2 SEMs of Charcoal Activated Carbon

Figure 3.10 and Figure 3.11 showed SEMs of charcoal activated carbon under 100× and 500× magnifications where closer view of surface area can be observed.

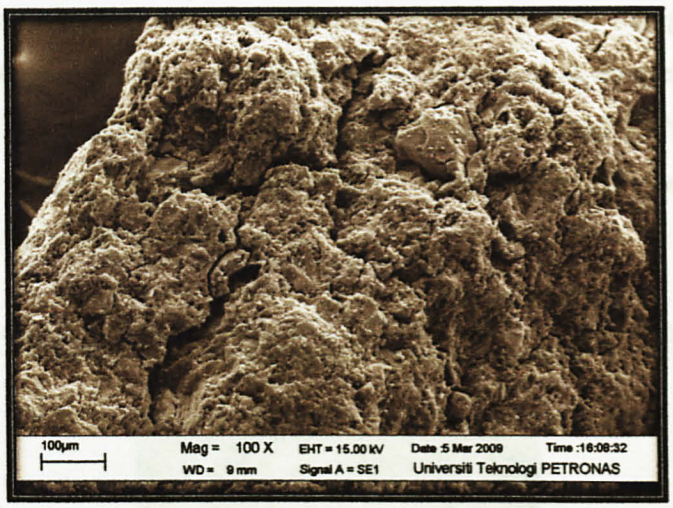


Figure 3.10 Charcoal activated carbon under 100× magnifications

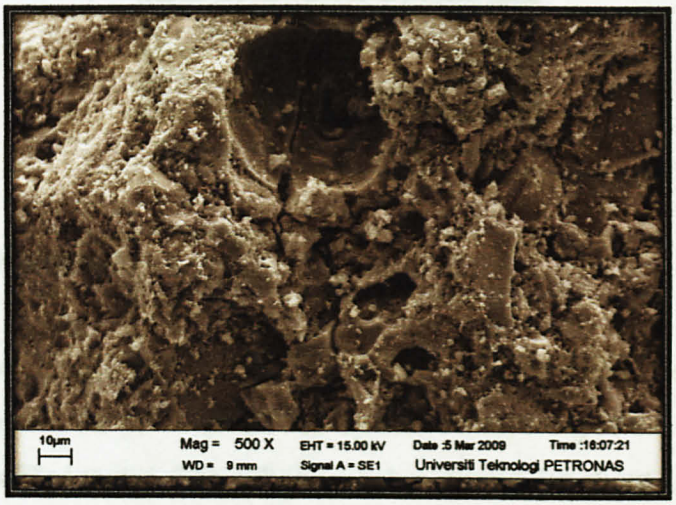


Figure 3.11 Charcoal activated carbon under 500× magnifications

3.6 PHYSICOCHEMICAL CHARACTERISTICS OF ACTIVATED CARBON

3.6.1 Ash Content

The ash content of coconut coir activated carbon is assessed by using muffle furnace where approximately 1 g of the activated carbon is burned at temperature of 900°C. As usual, the initial weight and final weight of the activated carbon is measured before and after the test. The percentage of ash content in the activated carbon can be calculated as shown in Equation 3-1.

$$\%\ of\ Ash\ Content = \frac{Weight\ of\ Ash}{Weight\ of\ original\ sample} \times 100\% \qquad (3\text{-}1)$$

Figure 3.12 Muffle furnace

3.6.2 pH Measurement

The pH of aqueous solution typically is measured using pH meter. As for the coconut coir activated carbon, the pH is quantified by immersing 1.0 g of the activated carbon in 100 mL of distilled water. The solution is then stirred for about 1 hour before the pH of slurry is measured.

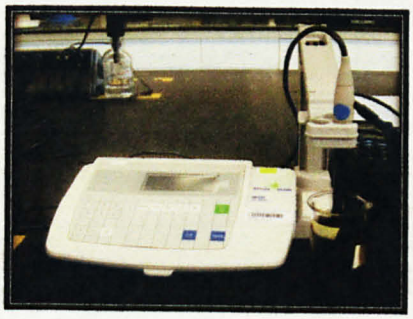


Figure 3.13 pH meter

3.7 ADSORPTION STUDY

3.7.1 Batch study

For adsorption studies, batch experiments were carried out by shaking 100 mL of dye solution using orbital shaker (see Figure 3.14) where initial amount of 0.5 g of coconut coir activated carbon is added in glass stoppered conical flasks at a temperature of 20°C at the rate of 150 rpm. The dye solutions used in this test were varied from concentration of 5 mg/L to 40 mg/L for both reactive dyes. During the analysis, effect of various parameters such as initial concentration, contact time, pH and adsorbent dose on the adsorption process was investigated. The progress of adsorption during the experiments was determined by removing flasks after desired contact time, centrifuging and analyzing the supernatant spectrophotometrically for dye concentration. Whatman No. 1 filter paper was used to filter the solution at each one hour interval throughout the test. As for the pH analysis, 0.1 N NaOH and 0.1 N HCl were used to adjust the pH to desire figure.

Figure 3.14 Orbital shaker

In batch studies, progress of adsorption was determined by calculating dye uptake to observe the percentage of dye removal in each test. The formula in obtaining dye uptake is shown in Equation 3-2.

$$Dye\ uptake\ (\%) = \frac{(C_0 - C_1)}{C_0} \times 100\% \quad (3\text{-}2)$$

where C_0 is the initial concentration and C_1 is the final concentration of the dye by referring to Standard Curve graph based on the absorbance measured using spectrophotometer.

3.7.2 Adsorption Isotherm

The adsorption isotherm was conducted soon after the batch studies were completed. It was carried out by using ten different concentrations of both reactive dyes varying from 10 to 100 mg/L. Contact time, pH and carbon dosage for both dyes were determined from the optimum condition in batch studies. The final solution was then measured spectrophotometrically for dye absorbance.

To compare the effectiveness of prepared coconut coir activated carbon, the same adsorption isotherm test was conducted for both dyes using charcoal activated carbon. The data obtained from both experiments was fitted and compared with Langmuir and Freundlich models.

Figure 3.15 Adsorption isotherm studies

3.8 GANTT CHART

A graphical representation of the completed and planned task or activities conducted for both semester of Final Year Project I and II (FYP) were summarized in the following bar charts:

Table 3.4 Gantt chart for Final Year Project I

No.	Detail	Week														
		1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
1.	Selection of Project Topic															
2.	Submission of Proposal															
3.	Weekly Meeting with Supervisor															
4.	Submission of Journal Summary															
5.	Project Work															
	▪ Study on journals/books															
	▪ Preparation of coconut coir activated carbon															
6.	Seminar/Workshop															
7.	Submission of Progress Report															
8.	Project Work continue															
	▪ Preparation of coconut coir activated carbon															
9.	Submission of Interim Report Final Draft															
10.	Oral Presentation															

Legend:

Table 3.5 Gantt chart for Final Year Project II

No.	Detail	Week														
		1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
1.	Project Work continue															
	▪ Preparation of coconut coir activated carbon															
	▪ Lab test for physicochemical characteristics															
	▪ Batch studies															
2.	Submission of Combined Progress Report															
3.	Weekly Meeting with Supervisor															
4.	Project Work continue															
	▪ Adsorption studies															
5.	Seminar/Workshop															
6.	Poster Presentation/Exhibition (EDX)															
7.	Submission of Dissertation															
8.	Oral Presentation															

Legend:

Completed task | Progress/Process | Suggested milestone | Mid semester break

3.9 TOOLS

3.9.1 Spectrophotometer

Spectrophotometer versatility allows the best wavelength of light to be used at all times. The optimum wavelength was determined at any time by establishing a spectral transmission curve. This was an essential part of research aimed at developing new methods of colourimetric analysis. The curve was established by making a series of observations of light transmission at several different wavelengths of light while using a typical coloured solution in the cell. The wavelength that absorbed to the greatest extent was the optimum wavelength to use.

Figure 3.16 Spectrophotometer

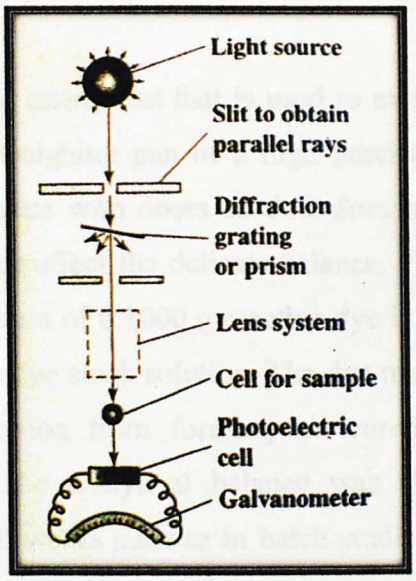


Figure 3.17
Schematic diagram of a spectrophotometer
(Source: Sawyer et. al., 2003)

3.9.2 Fume Cupboard

A fume hood or fume cupboard is a large piece of scientific equipment common to chemistry laboratories designed to limit a person's exposure to hazardous and/or unpleasant fumes. The principle is the same for all units; air is drawn in from the front of the cabinet by a fan, and either expelled outside the building or made safe through filtration and fed back into the room. For this work, fume cupboard was used while mixing concentrated sulfuric acid with coconut coir and when diluting 10% of hydrochloric acid, as the vapor was harmful to eyes and bad to the respiratory system if inhaled.

Figure 3.18 Fume cupboard

3.9.3 Analytical Balance

An analytical balance is an instrument that is used to measure mass to a very high degree of precision. The weighing pan of a high precision analytical balance are inside a transparent enclosure with doors so dust does not collect and so any air currents in the room do not affect the delicate balance. The analytical balance was used to measure exact amount of 0.1000 g reactive dye in powdered form, which to be used for composing the dye stock solution. The dye must be at room temperature to prevent natural convection from forming air currents inside the enclosure, affecting the weighing. The analytical balance was also used to measure the adsorbent for experimental works such as in batch studies and adsorption isotherm models.

Figure 3.19 Analytical balance

3.9.4 Glassware

Laboratory glassware refers to a variety of equipment, traditionally made of glass, used for scientific experiments in the laboratories. Glass is used for some applications because it is relatively inert, transparent, more heat-resistant than some plastic up to a point, and relatively easy to customize. Borosilicate glasses, formerly called Pyrex are often used because less subject to thermal stress. As for this research, such glassware were used for a wide variety of functions which includes volumetric measuring during dilution of dye, holding or storing chemicals or samples (sulphuric acid, sodium bicarbonate, etc.), mixing or preparing chemical solutions with the raw coir, and testing the dye absorbance spectrophotometrically.

3.10 SAFETY PRECAUTIONS

The Occupational Safety and Health Administration (OSHA) stated the students have to comply with the requirements of the Hazard Communication Standard (HCS: 29CFR 1910.1200). HCS insist the students to have access to a list of all the chemicals present in the laboratories and Material Safety Data Sheets (MSDS) are available for each chemical in the lab. Besides, chemical containers must be properly labeled and hazards must be listed. Also, students must be trained in the proper handling of the chemicals before conducting any experiments.

3.10.1 Personal Protective Equipment (PPE)

During the experimental works, safety precautions were taken at all times to avoid any risk of unwanted accident from happened in the environmental laboratory of UTP Civil Engineering Department. Personal Protective Equipment (PPE) such as protective clothing (laboratory coat), gloves, eye protection (goggles), safety footwear and masks were intended to be worn during any laboratory session or if necessary depending on the laboratory works as to protect against one or more risks to health and safety.

3.10.2 Chemical Reaction

Strong acid and bases such as sulfuric acid, hydrochloric acid and sodium bicarbonate used during the experiments were corrosive and could cause serious injury even on short exposure. If spilled on skins, the solution could cause a chemical burn. Besides, they were very harmful to eyes as well. If accidentally breathe in a big whiff of vapors, some will feel a burning in nasal and respiratory passages. Thus, the solution must be handled with great care so as not to spill or inhaled the vapors. Protective clothing and shoes were worn during laboratory works while goggles and gloves were worn if necessary. In case of emergency because of spilling the solution, affected area was rinsed with lots of water and medical attention was sought if the affected area remains more than slightly red after the rinsing period.

3.10.3 Glassware

Common sense was used when handling glassware. It was kept away from the edge of the bench top and to prevent from falling over, reaction flask and the suction flask were securely clamped to a ring stand. Each piece of glassware was checked for hairline or star cracks before used. For instance, when handling a distillation, each piece of glassware needs to be securely clamped. If a piece of glassware was accidentally broken, it was not left in the sink or on the bench top because someone

may inadvertently get cut. A brush and dustpan were used to sweep up the broken glass while wearing thick gloves. Broken glassware was placed in one of the "Broken Clean Glassware" containers located in the labs. Cuts can be prevented by wearing thick gloves, especially while washing glassware. Feet were protected by wearing closed-toed shoes, not only to protect from dropped glassware, but also to protect from broken pieces of glass which may be on the floor from a previous lab section. Goggles were worn to protect eyes from flying broken glassware.

Figure 3.20 Glassware

3.10.4 Devices

This research also deals with electrical appliances use in the laboratories such as air oven, fixed bed activation unit, muffle furnace, spectrophotometer, grinding machine, etc. A heavy glove was worn to prevent thermal burn on skin when taking out samples from air oven or furnace. Grinding machine was carefully used to avoid electrical shock by periodically checking the cord or plug and ensure it was not damaged or frayed. The plug also disconnected from the socket when it was not used and water was always kept away from any electrical appliances. During emergency regarding thermal burns, affected area was covered with cool water or ice. After a while, pain-relieving cream was applied and medical attention was sought if the burn looks like it was more than just a reddening of the skin.

CHAPTER 4
RESULTS AND DISCUSSION

4.1 DYE CONCENTRATION & ABSORBANCE

Two types of reactive dyes namely Reactive Red 180 and Reactive Blue 19 were investigated in this study. After testing the dye solutions spectrophotometrically, the results of absorbance for each reactive dye were plotted in the following figures.

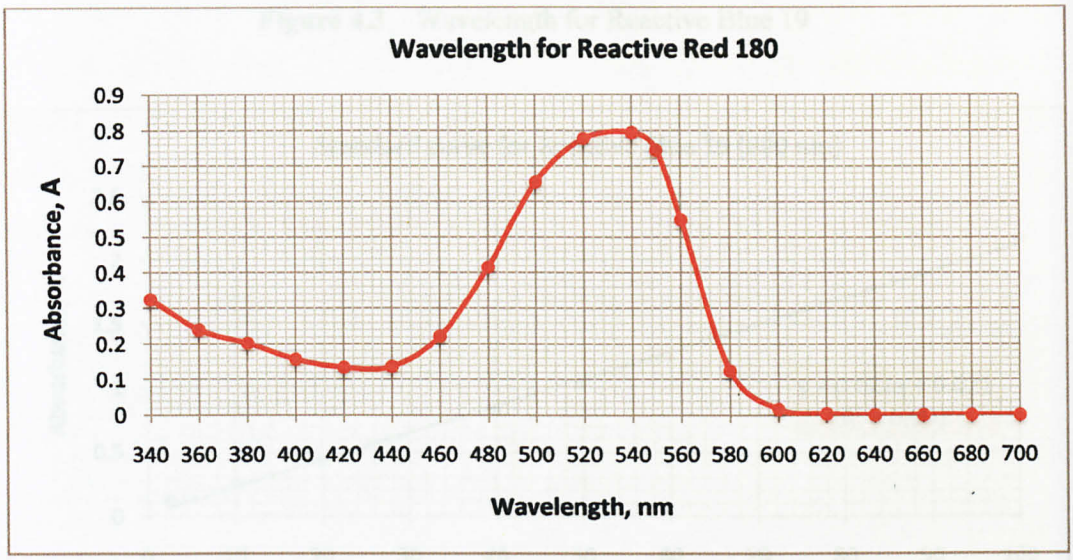


Figure 4.1 Wavelength for Reactive Red 180

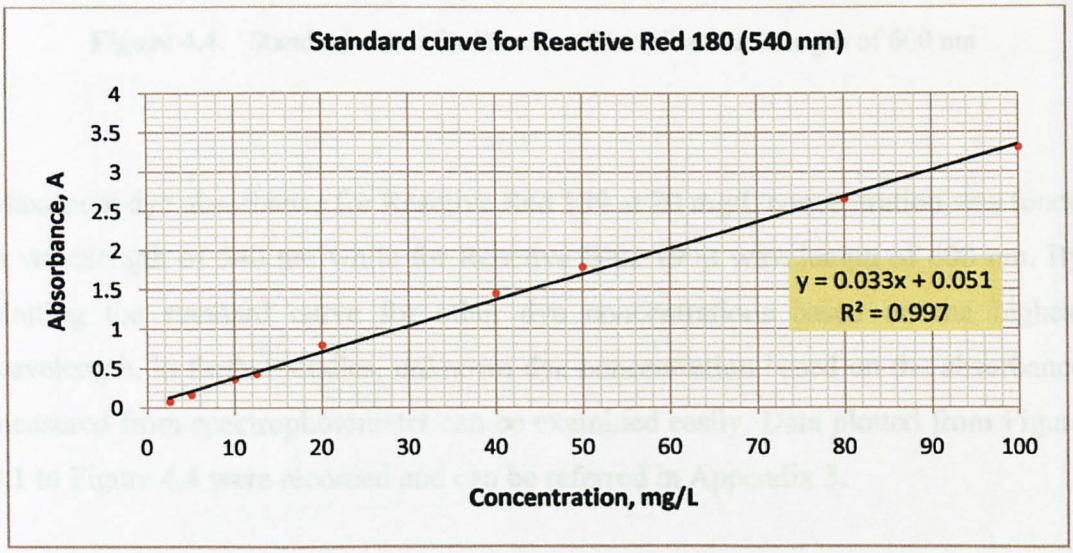


Figure 4.2 Standard curve for Reactive Red 180 at wavelength of 540 nm

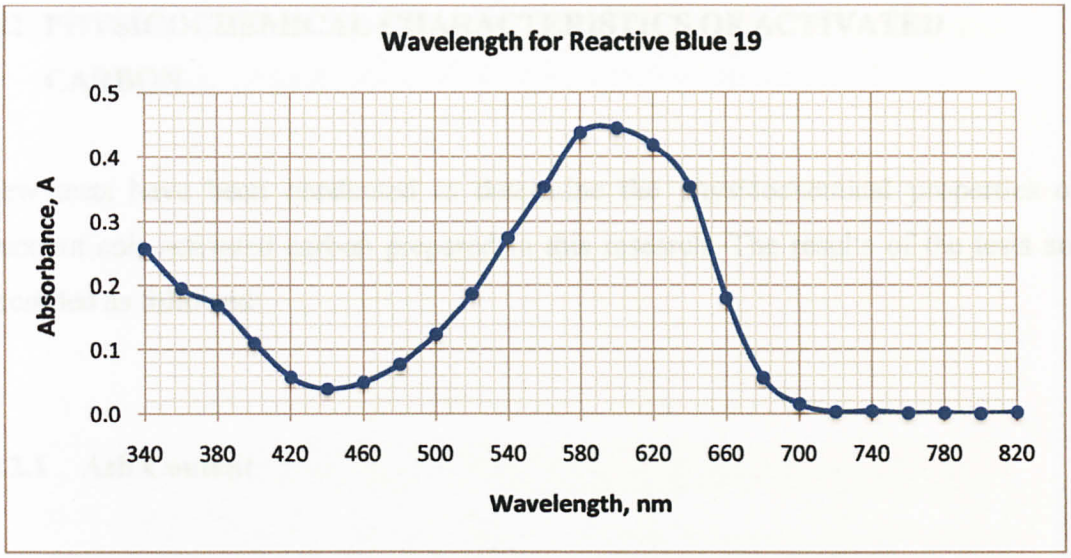


Figure 4.3 Wavelength for Reactive Blue 19

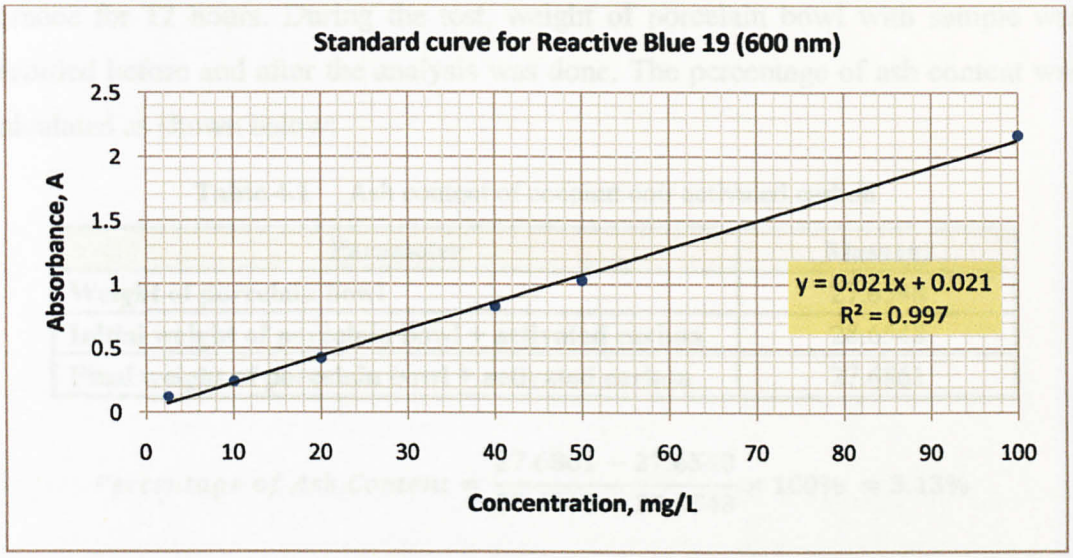


Figure 4.4 Standard curve for Reactive Blue 19 at wavelength of 600 nm

Maximum dye absorbance for Reactive Red 180 at 20 mg/L concentration was found at wavelength of 540 nm while for Reactive Blue 19 at wavelength of 600 nm. By plotting the standard curve for other dye concentrations based on the highest wavelength, in further studies, unknown dye concentration based on the absorbance measured from spectrophotometer can be examined easily. Data plotted from Figure 4.1 to Figure 4.4 were recorded and can be referred in Appendix 3.

4.2 PHYSICOCHEMICAL CHARACTERISTICS OF ACTIVATED CARBON

Few tests have been conducted to determine the physicochemical properties of coconut coir activated carbon prepared in this research. The results of the tests are recorded as followed:

4.2.1 Ash Content

Ash content in the coconut coir activated carbon was measured using 125 mL porcelain bowl, where the activated carbon was burned at 900°C using muffle furnace for 12 hours. During the test, weight of porcelain bowl with sample was recorded before and after the analysis was done. The percentage of ash content was calculated as shown below:

Table 4.1 Ash content of coconut coir activated carbon

Parameter	Mass (g)
Weight of porcelain bowl	27.6548
Initial weight of porcelain bowl + activated carbon	28.6548
Final weight of porcelain bowl + activated carbon	27.6861

$$Percentage\ of\ Ash\ Content = \frac{27.6861 - 27.6548}{28.6548 - 27.6548} \times 100\% = 3.13\%$$

4.2.2 pH Measurement

Test to determine the pH of coconut coir activated carbon was conducted three times using pH meter. The data for each test were recorded as followed:

Table 4.2 pH of coconut coir activated carbon

Sample	pH
1	6.765
2	6.438
3	6.574

From the data, mean value of pH for coconut coir activated carbon was at 6.59.

4.2.3 Comparison with Coconut Coir Pith Activated Carbon (Santhy and Selvapathy, 2006)

The results of these few analysis of coconut coir activated carbon was summarized and compared with the coconut coir pith activated carbon prepared by Santhy and Selvapathy (2006) in their research.

Table 4.3 Coconut coir activated carbon vs. coconut coir pith activated carbon

Characteristics	Coconut Coir AC	Coconut Coir Pith AC
Ash content (%)	3.13	2.93
pH	6.59	6.50

From both analysis, characteristics of ash content and pH for coconut coir activated carbon and coconut coir pith activated carbon were relatively the same with not much difference to compare.

4.3 ADSORPTION STUDY

4.3.1 Batch Study

Batch studies were carried out to examine the removal efficiency of prepared coconut coir activated carbon. During the analysis, effect of various parameters such as initial concentration, contact time, pH and adsorbent dose on the adsorption process was investigated for an interval of one hour or until equilibrium had ceased. The progress of adsorption was determined by removing containers after desired contact time, centrifuging and analyzing the supernatant spectrophotometrically for dye absorbance.

4.3.1.1 *Effect of initial concentration and contact time*

Since molecular structures of Reactive Red 180 and Reactive Blue 19 were different, concentrations used for both reactive dyes also differ in order to determine the effect of initial concentration and contact time. The effect of initial concentration and contact time for the progress of adsorption during the experiment for both dyes and coconut coir activated carbon were concluded in the following tables and figures:

Table 4.4 Effect of contact time on removal of Reactive Red 180

Contact time (h)	Initial concentration = 5 mg/L		Initial concentration = 10 mg/L	
	Final concentration (mg/L)	% Removal	Final concentration (mg/L)	% Removal
1	1.70	65.92	5.57	44.30
2	1.37	72.65	4.63	53.67
3	1.12	77.58	4.58	54.18
4	1.08	78.48	4.53	54.68
Contact time (h)	**Initial concentration = 20 mg/L**		**Initial concentration = 40 mg/L**	
	Final concentration (mg/L)	**% Removal**	**Final concentration (mg/L)**	**% Removal**
1	13.79	31.03	33.81	15.47
2	13.14	34.28	31.24	21.89
3	12.85	35.77	31.22	21.96
4	12.68	36.59	30.88	22.91

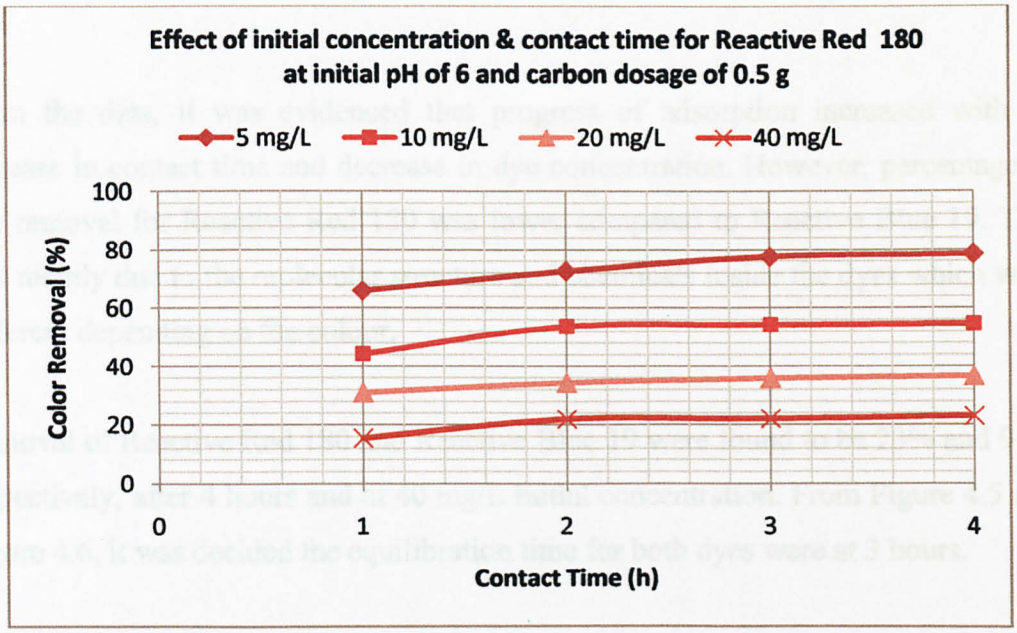


Figure 4.5 Effect of initial concentration and contact time on the adsorption of Reactive Red 180 by coconut coir activated carbon

Table 4.5: Effect of contact time on removal of Reactive Blue 19

Contact time (h)	Initial concentration = 20 mg/L		Initial concentration = 40 mg/L	
	Final concentration (mg/L)	% Removal	Final concentration (mg/L)	% Removal
1	5.17	74.13	27.28	31.80
2	1.99	90.05	6.76	83.11
3	1.49	92.54	4.52	88.70
4	1.49	92.54	3.63	90.93

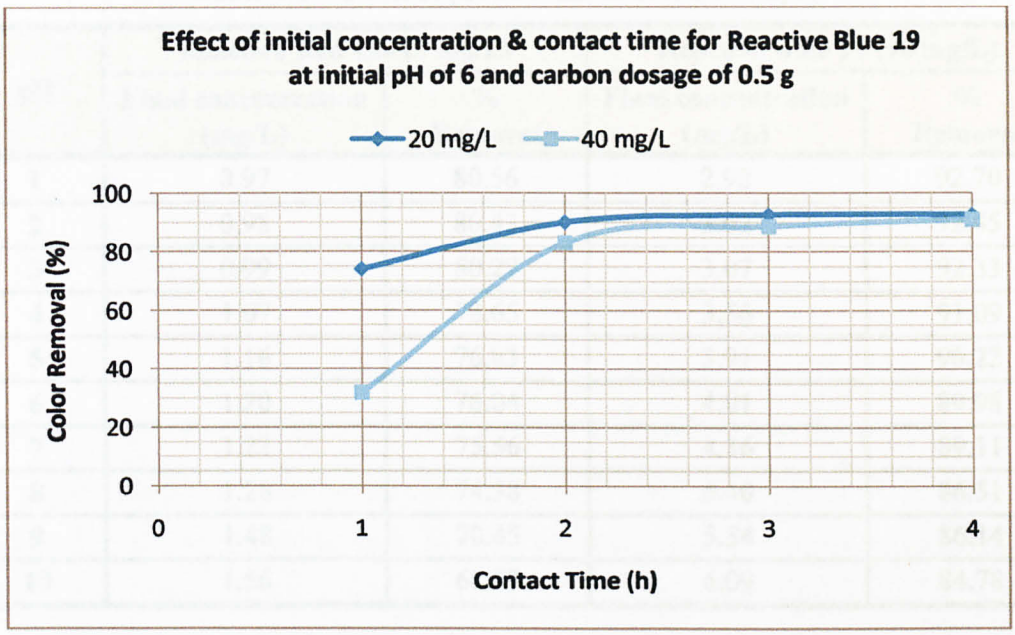


Figure 4.6 Effect of initial concentration and contact time on the adsorption of Reactive Blue 19 by coconut coir activated carbon

From the data, it was evidenced that progress of adsorption increased with an increase in contact time and decrease in dye concentration. However, percentage of dye removal for Reactive Red 180 was lower compared to Reactive Blue 19. This was mainly due to the molecular structure and chemicals inside the dyes which were different depending on the colour.

Removal of Reactive Red 180 and Reactive Blue 19 were found to be 23% and 91% respectively, after 4 hours and at 40 mg/L initial concentration. From Figure 4.5 and Figure 4.6, it was decided the equilibration time for both dyes were at 3 hours.

4.3.1.2 *Effect of pH*

In order to determine desirable pH for both dyes, 0.1 N NaOH and 0.1 N HCl were used. The concentrations of dyes used for Reactive Red 180 was 5 mg/L while for Reactive Blue 19 was 40 mg/L with pH varied from 1 to 10 for each concentrations. The results obtained from this test were summarized in Table 4.6.

Table 4.6 Effect of pH on removal of reactive dyes

pH	Reactive Red 180 (5 mg/L)		Reactive Blue 19 (40 mg/L)	
	Final concentration (mg/L)	% Removal	Final concentration (mg/L)	% Removal
1	0.97	80.56	2.92	92.70
2	0.98	80.43	3.02	92.45
3	0.99	80.27	3.07	92.33
4	1.07	78.65	3.56	91.09
5	1.16	76.83	3.91	90.22
6	1.20	76.04	4.01	89.98
7	1.22	75.56	4.36	89.11
8	1.28	74.38	5.40	86.51
9	1.48	70.45	5.54	86.14
10	1.56	68.77	6.09	84.78

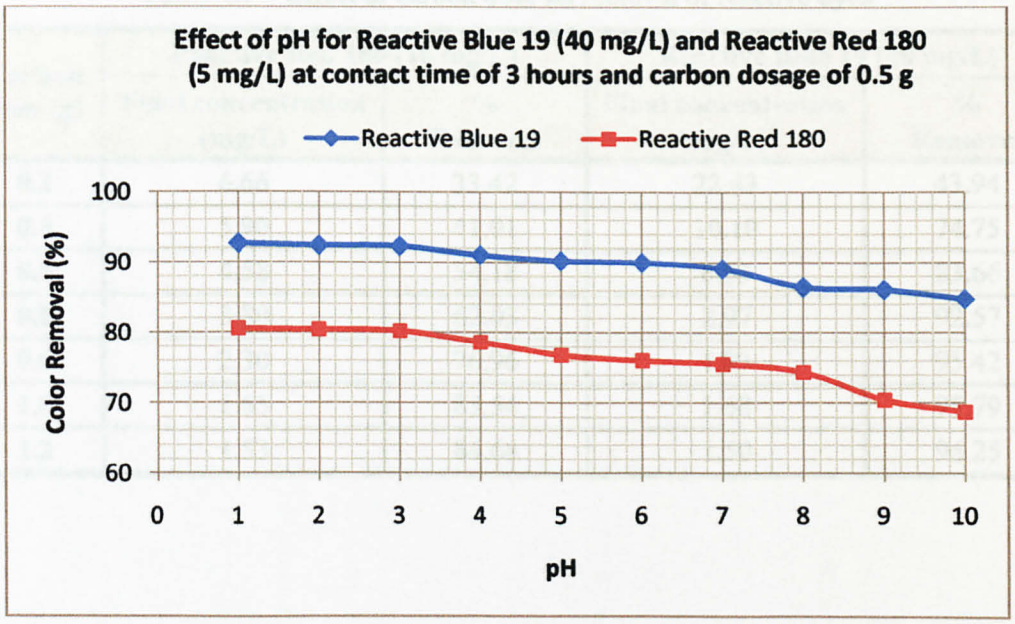


Figure 4.7 Effect of pH on the adsorption of reactive dyes by coconut coir activated carbon

Figure 4.7 showed the effect of pH on the adsorption of reactive dyes with coconut coir activated carbon. The maximum removal of dyes was found in the acidic pH ranges from 1-3. The pH value of the dye concentration probably effects the adsorption process and mainly on the adsorption capacity.

Santhy and Selvapathy (2006) also indicate similar observations where it was decided to maintain a pH of 3.0, at which the removal was optimum. They concluded that positive charges on the surface increased as the pH of the adsorption solution was lowered. This behavior would attract the negatively charged functional group located in the reactive dyes.

4.3.1.3 Effect of carbon dose

Dyes in the concentration of 10 mg/L for Reactive Red 180 and 40 mg/L for Reactive Blue 19 were used to investigate the effect of carbon dose where the amount of coconut coir activated carbon added in each container were varied from 0.2 g to 1.2 g. The pH value for both dyes at volume of 100 mL was maintained at pH 3.0. The data recorded from the test can be referred as followed:

Table 4.7 Effect of carbon dose on removal of reactive dyes

Carbon dose (g)	Reactive Red 180 (10 mg/L)		Reactive Blue 19 (40 mg/L)	
	Final concentration (mg/L)	% Removal	Final concentration (mg/L)	% Removal
0.2	6.66	33.42	22.43	43.94
0.4	5.90	41.01	10.10	74.75
0.5	4.58	54.18	6.53	83.66
0.6	3.80	62.03	2.97	92.57
0.8	2.30	76.96	1.83	95.42
1.0	1.65	83.54	1.68	95.79
1.2	1.53	84.68	1.50	96.25

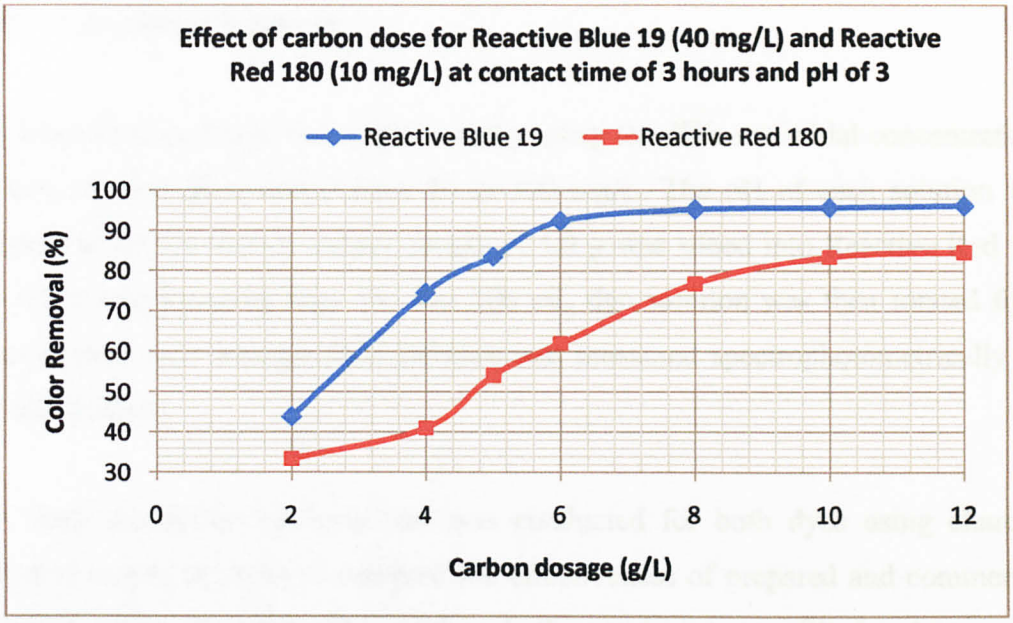


Figure 4.8 Effect of carbon dose on the adsorption of reactive dyes by coconut coir activated carbon

It was observed from the graph that in both cases, the dye uptake increased with increase amount of coconut coir activated carbon added to the flask. After 3 hours, colour removal of about 93% was achieved at 6 g/L for Reactive Blue 19 and nearly 84% for Reactive Red 180 at 10 g/L. The rate of adsorption for both dyes was difference principally due to the composition of the dyes; where the molecular structures and chemicals content were varied from one another. Therefore, the dye uptake for both colours was also difference. The optimum condition obtained from batch studies are summarized in the following table and these numerical figures will be used in adsorption studies:

Table 4.8 Optimum condition for contact time, pH and carbon dosage

Parameter	Reactive Red 180	Reactive Blue 19
Contact time	3 hours	3 hours
pH	3	3
Carbon dosage	10 g/L	6 g/L

4.3.2 Adsorption Isotherm

The adsorption isotherm was carried out by using ten different initial concentrations of both reactive dyes varied from 10 to 100 mg/L. The pH of each solution was adjusted at pH 3.0 with a carbon dosage of 1.0 g was added into Reactive Red 180 and 0.6 g into Reactive Blue 19. The 100 mL dye solution was then rotated for 3 hours contact time and the final solution was measured spectrophotometrically for dye absorbance.

The same adsorption isotherm test was conducted for both dyes using charcoal activated carbon in order to compare the effectiveness of prepared and commercial activated carbon. The data obtained from both experiments was fitted and compared with Langmuir and Freundlich models. The calculation to determine both adsorption isotherms were attached in Appendix 4.

4.3.2.1 The Langmuir Adsorption Isotherm

Below figures indicate the adsorption isotherm for both reactive dyes; best fitted using Langmuir adsorption isotherm.

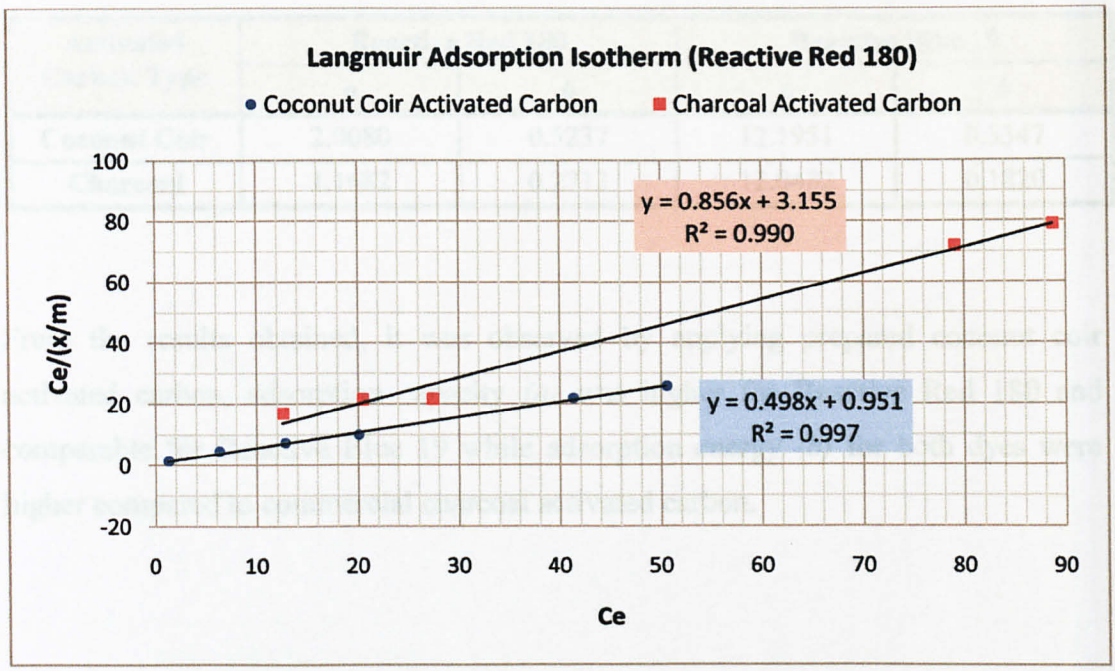


Figure 4.9 Langmuir adsorption isotherm for Reactive Red 180

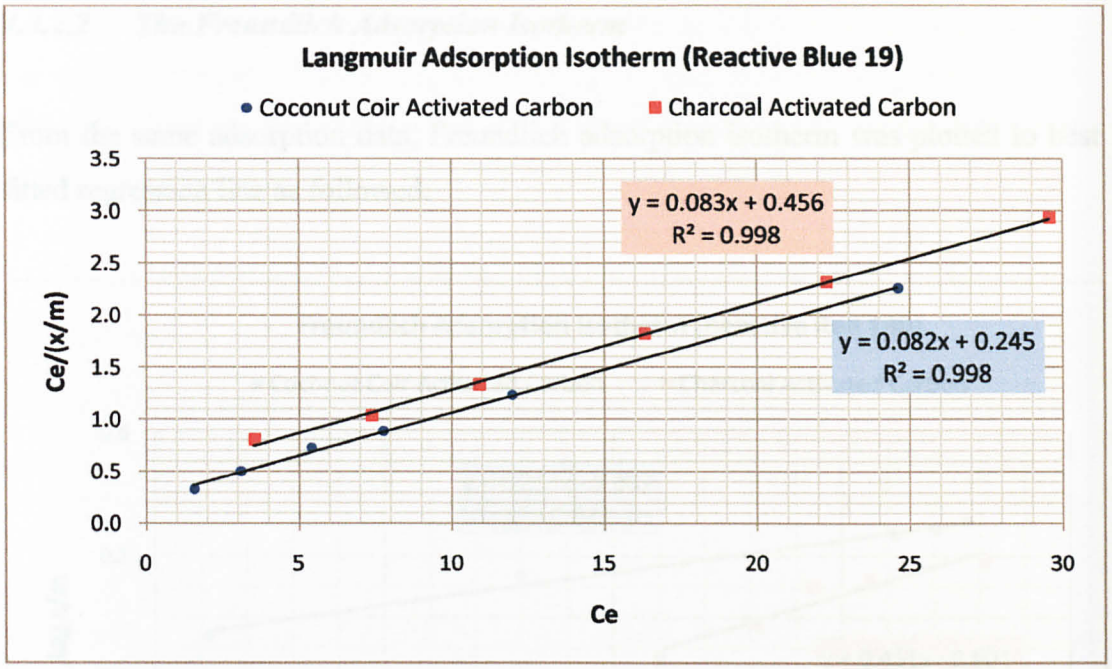


Figure 4.10 Langmuir adsorption isotherm for Reactive Blue 19

By referring to Equation 2-2 and comparing with the equation on the above figures, value of constant for both dyes were calculated. The value of *a* indicated the number of moles of solute adsorbed per unit weight of adsorbent in forming a complete monolayer on the surface and *b* was a constant related to energy of adsorption.

Table 4.9 Empirical constant of Langmuir adsorption isotherm

Activated Carbon Type	Reactive Red 180		Reactive Blue 19	
	a	*b*	*a*	*b*
Coconut Coir	2.0080	0.5237	12.1951	0.3347
Charcoal	1.1682	0.2713	12.0482	0.1820

From the results obtained, it was observed by applying prepared coconut coir activated carbon, adsorption capacity *(a)* was higher for Reactive Red 180 and comparable for Reactive Blue 19 while adsorption energy *(b)* for both dyes were higher compared to commercial charcoal activated carbon.

4.3.2.2 *The Freundlich Adsorption Isotherm*

From the same adsorption data, Freundlich adsorption isotherm was plotted to best fitted regression line as followed:

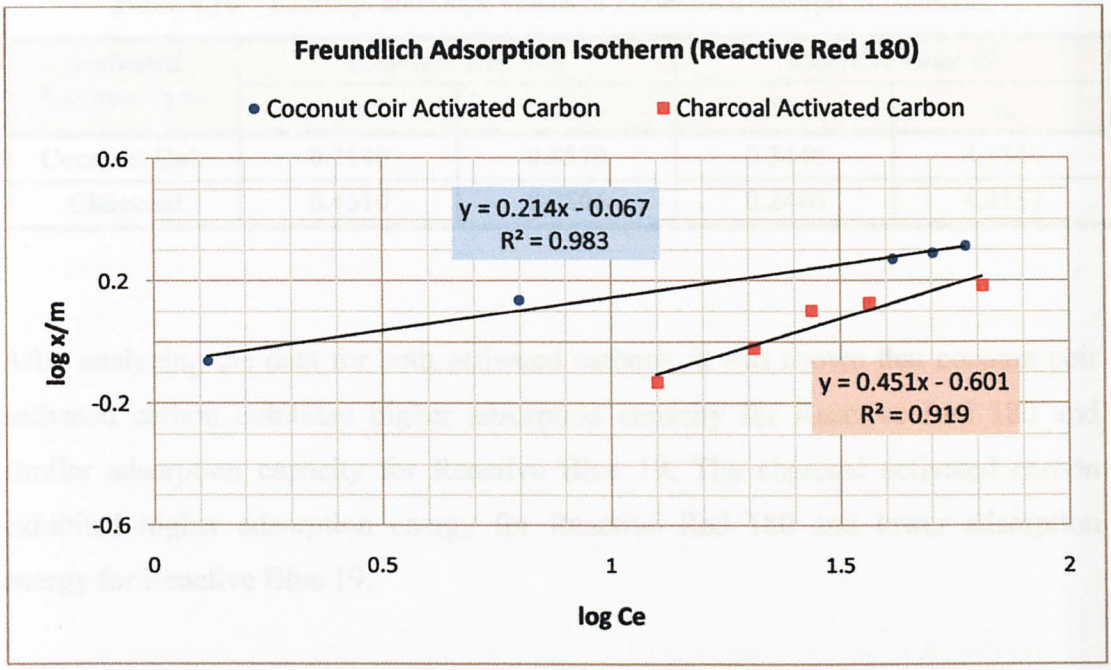


Figure 4.11 Freundlich adsorption isotherm for Reactive Red 180

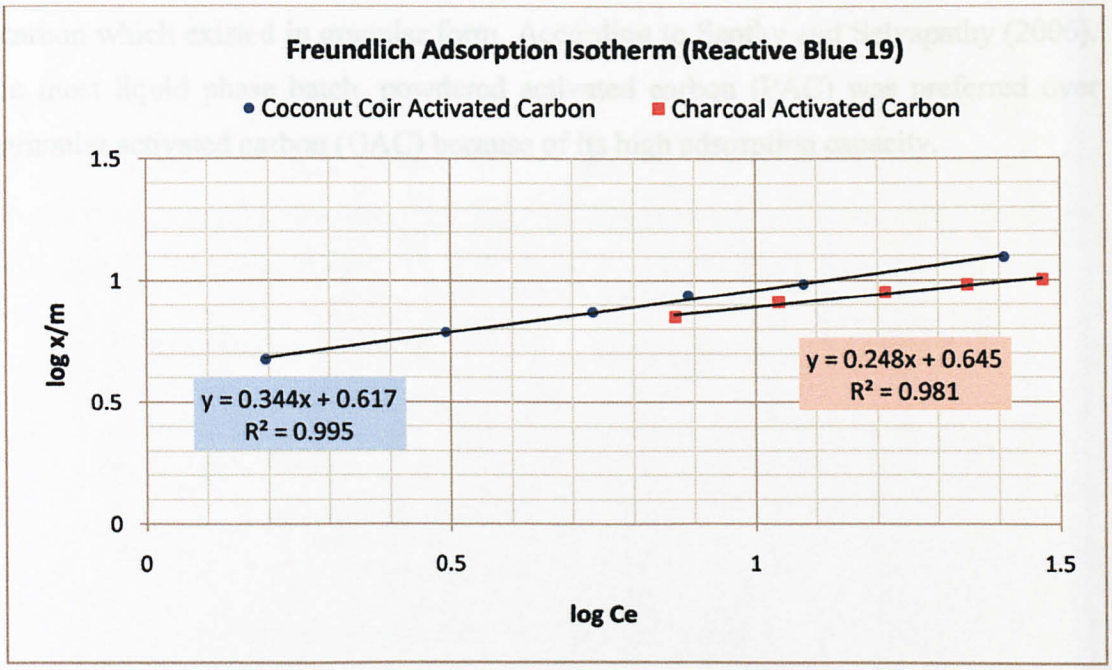


Figure 4.12 Freundlich adsorption isotherm for Reactive Blue 19

The value of K (intercept) and 1/n (slope) are roughly an indicator of adsorption capacity and adsorption energy of the activated carbon. By referring to Equation 2-4 and comparing with equation in above figures, value of K and 1/n for both dyes were calculated and recorded as in following table:

Table 4.10 Intercept and slope values of Freundlich adsorption Isotherm

Activated Carbon Type	Reactive Red 180		Reactive Blue 19	
	1/n	K	1/n	K
Coconut Coir	0.2140	0.8570	0.3440	4.1340
Charcoal	0.4510	0.2506	0.2480	4.4157

After analyzing the data for both activated carbons, it was shown that coconut coir activated carbon exhibited higher adsorption capacity for Reactive Red 180 and similar adsorption capacity for Reactive Blue 19. The charcoal activated carbon exhibited higher adsorption energy for Reactive Red 180 and lower adsorption energy for Reactive Blue 19.

By comparing the use of coconut coir activated carbon and charcoal activated carbon in colour removal of both dyes, it was shown that coconut coir activated carbon was more effective. This was probably due to the physical form of charcoal activated carbon which existed in granular form. According to Santhy and Selvapathy (2006), in most liquid phase batch, powdered activated carbon (PAC) was preferred over granular activated carbon (GAC) because of its high adsorption capacity.

CHAPTER 5

CONCLUSION AND RECOMMENDATION

The present research indicates that activated carbon prepared from coconut coir is a suitable adsorbent for removal of reactive dyes from aqueous solution. Lignocellulosic contents of coconut coir and physicochemical characteristics of the coconut coir activated carbon are suitable factors which can enhance the rate of adsorption process. In batch studies, it was shown that dye uptake increased with an increase in contact time and carbon dosage and decrease in dye concentration. In adsorption isotherm studies, the data were fitted to the Langmuir and Freundlich models where it revealed that the prepared coconut coir activated carbon was more effective compared to the commercial charcoal activated carbon. Thus, activated carbon prepared from coconut coir proved as one of the successful alternative sorbents to remove reactive dyes from aqueous solution.

For future works, it is recommended to test for other parameters to determine the physicochemical characteristics of coconut coir activated carbon such as moisture content (%), matter soluble in water and acid (%), iron exchange capacity (meq/g), apparent density (g/cm^3) and surface area (m^2/g).

Few other experiments should be conducted by using real effluent so that the effectiveness of applying coconut coir activated carbon to treat textile wastewater can be observed. Below are the lists of experiments and test that should be investigated in further studies:

1) Kinetics of adsorption
    - Effect of anions
2) Column studies
    - Effect of flow rate
    - Effect of bed depth
    - Bed Depth Service Time (BDST) analysis
    - Recycling of carbon bed
    - Removal of reactive dyes from textile mill effluent

REFERENCES

Allen S. J., Koumanova B., 2005. *Decolourisation of Water/Wastewater using Adsorption.* Journal of the University of Chemical Technology and Metallurgy, 40, 3, 2005, 175-192.

Allen S. J., Khader K. J. H., McKay G., 1988. Environmental Pollution, 52, 39-53.

Al-Degs Y., Khraisheh M. A. M., Allen S. J., Ahmad N. A., 2000. *Effect of Carbon on the Removal of Reactive Dyes from Textile Effluent,* Water Research, 34 (3), 927-935.

Banat IM, Nigam P., Singh D., Marchant R., 1996. *Microbial decolourization of textile dyes containing effluents; a review.* Bioresource Technology, 58, 217-227.

Carr K., 1995. *Reactive dyes, especially bi-reactive molecules, structure and synthesis. In: Peters, A. T., Freeman, H. S. (Eds.), Modern Colourants: Synthesis and Structure.* Blackie Academic and Professional, London, pp. 87-122.

Dan T. K., 1993. *Development of light weight building bricks using coconut pith.* Industrial Coconut Journal, 23, 12-19.

DIN 38 404, 1991. *German Methods for the Examination of Water, Wastewater and Sludge, Physical and Physical-Chemical Parameters (Group C), Determination of Colour.* Deutches Institute for Normung e.v., Berlin, pp. 1-7.

Frank G., Frank H, Wilhelm O., 1994. *Ozonation – an important technique to comply with new German laws for textile wastewater treatment.* Water Science and Technology 30, 25-263.

Garg, V. K., Gupta R., Yadav, A.B., Kumar R., 2003. *Dye Removal from Aqueous Solution by Adsorption on Treated Sawdust.* Bioresource Technology, 89, 121-124.

Garg V. K., Rakesh Kumar, Renuka Gupta, 2004. *Removal of Malachite Green Dye from Aqueous Solution by Adsorption using Agro-Industry Waste: A Case Study of Prosopis Cineraria.* Dyes and Pigments, 62, 1-10.

Gregor K. H., 1991. *Oxidative Decolourisation of Textile Wastewater with Advanced Oxidation Processes. Chemical Oxidation – Technologies for the Nineties.* Technomic Publishing Corporation, Lanchester, pp. 161-193.

Kharaisheh, M. A. M., Al Degs, Y. S., Allen, S. T., Ahmad, M. N., 2002. *Elucidation on controlling steps of reactive dye adsorption on activated carbon.* Industrial and Engineering Chemistry Research, 41, 1651- 1657.

Lazearidis, N. K., Darapantsios, T. D., Geiogantas, D., 2003. *Kinetic analysis for the removal of a reactive dye from aqueous solution onto hydrotalcite by adsorption.* Water Research 37. 3023-3033.

Leon C. A., Solar J. M., Calemma V., Radovic L. R., 1992. *Evidence for the protonation of basal plane sites on carbon.* Carbon, 30 (5), 797-811.

Mckay G., 1982. *Adsorption of dye stuffs from aqueous solutions with activated carbon, Part I, Equilibrium and batch contact time studies.* Journal of Chemical Technology Biotechnology, 32, 759-772.

Metcalf & Eddy, Inc. revised by Tchobanoglous G., Burton F. L., Stensel H. D., 1994. *Wastewater Engineering - Treatment and Reuse.* McGraw Hill, New York.

Moreno-Castilla C., Carrasco-Marin F., Mueden A., 1997. *The creation of acid*

carbon surfaces by treatment with $(NH_4)_2S_2O_8$. Carbon, 35 (10-11), 1619-1626.
Namasivayam C., Dineshkumar M., Selvi K., Begam R. A., Vanathi T., Yamuna R. T., 2001. *Waster coir pith – a potential biomass for the treatment of dyeing wastewaters.* Biomass Bioenergy. 21, 477-483.
Netpradit, S. Thiravetyan, P., Towprayoon, S., 2003. *Evaluation of metal hydroxide sludge for reactive adsorption in a fixed-bed column system.* Water Research, 38, 71-78.
Parks G. A., 1965. Chemical Resource, 65, 177-198.
Pierce J., 1994. *Colour in textile effluents – the origins of the problem.* Journal of the Society of Dyers and Colourists, 110, 131-133.
Puri B. R., 1994. *Chemistry and physics of activated carbon.* Marcel Dekker, New York.
Ruthven D. M., 1984. *Principles of adsorption and adsorption processes.* Wiley International.
Santhy K., Selvapathy P., 2006. *Removal of Reactive Dyes from Wastewater by Adsorption on Coir Pith Activated carbon.* Bioresource Technology, 97, 1329-1336.
Sawyer C. N., McCarty P. L., Parlan G. F., 2003. *Chemistry for Environmental Engineering and Source.* The McGraw-Hill Companies Inc., New York.
Senthilkumaar S., Kalaamani P., Porkodi K., Varadarajan P. R., Subburaam C. V., 2006. *Adsorption of Dissolved Reactive Red Dye from Aqueous Phase onto Activated carbon Prepared from Agricultural Waste.* Bioresource Technology, 97, 1618-1625.
Slokar Y. M., Le Marechal M., 1998. *Methods of decoloration of textile wastewater dyes and pigments.* Dyes and Pigments, 37, 335-357.
Strickland A. F., Perkins W. C., 1995. *Decolorization of continuous dyeing wastewater by ozonation.* Textile Chemist and Colourist. 27, (11-15)
Sureshkumar M. V., Namasivayam C., 2007. *Adsorption Behavior of Direct Red 12B and Rhodamine B from Water onto Surfactant-Modified Coconut Coir Pith, Colloids and Surfaces A*: Physicochemical Engineering Aspects. 317, 277–283.
Suzuki M., 1990. *Adsorption Engineering.* Elsevier, Amsterdam.
Suzuki M., 1997. *Role of adsorption in water environment,* Water Science Technology. 35, 7. 1-11.
Weber, W. J. Jr., 1972. *Physicochemical Processes for Water Quality Control.* Wiley-Interscience.
Wong, L. C. Y., 2006. *Development of Malaysia's Agricultural Sector: Agriculture as an Engine of Growth?*, Institute of Strategic and International Studies (ISIS) Malaysia. 1-22.
Young, Lu., Yu, J., 1997. *Lignase-catalysed Decolourisation.* Water Research. 31, 1187-1193.

APPENDICES

APPENDIX 1

DILUTION FACTOR FOR

DYE STOCK SOLUTION OF 100 mg/L

APPENDIX 1: DILUTION FACTOR

Table A1 Dilution factor for 100 mg/L dye stock solution

Dye concentration to be obtained (mg/L)	Volume of stock solution to be added (mL)	Volume of distilled water to be added (mL)	Total volume of dye concentration (mL)
90	225	25	250
80	200	50	250
70	175	75	250
60	150	100	250
50	125	125	250
40	100	150	250
30	75	175	250
25	62.5	187.5	250
20	50	200	250
15	37.5	212.5	250
12.5	31.25	218.75	250
10	25	225	250
5	12.5	237.5	250
2.5	6.25	243.75	250

APPENDIX 2

PHOTOGRAPHS ON PREPARATION OF COCONUT COIR ACTIVATED CARBON

APPENDIX 2: PHOTOGRAPHS ON PREPARATION OF COCONUT COIR ACTIVATED CARBON

Figure A1 Coconut coir after ground and washed

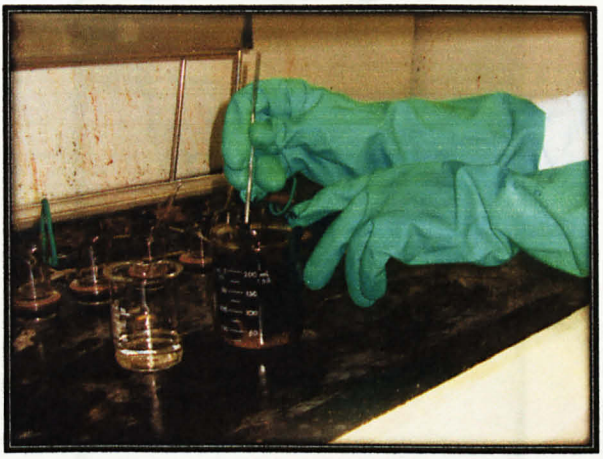


Figure A2 Coconut coir mixed with H_2SO_4

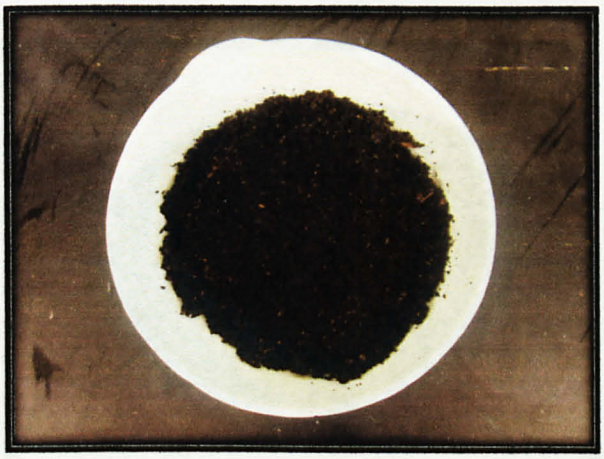


Figure A3 Char after mixed with H_2SO_4 and dried

Figure A4 Char washed with sodium bicarbonate

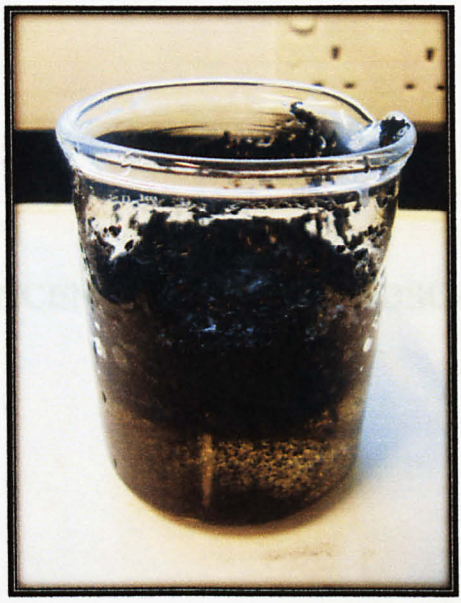


Figure A5 Carbon soaked in 10% HCl

Figure A6 Final product – coconut coir activated carbon

APPENDIX 3

DYE CONCENTRATION AND ABSORBANCE DATA SHEET

APPENDIX 3: DYE CONCENTRATION AND ABSORBANCE

C. I. REACTIVE RED 180

Table A2 Wavelength and dye absorbance at 20 mg/L

Wavelength (nm)	Dye absorbance at 20 mg/L
340	0.325
360	0.240
380	0.202
400	0.157
420	0.134
440	0.137
460	0.222
480	0.415
500	0.653
520	0.777
540	0.794
550	0.744
560	0.549
580	0.124
600	0.017
620	0.004
640	0.001
660	0.001
680	0.001
700	0.001

Table A3 Dye concentration and dye absorbance (540 nm)

Dye Concentration (mg/L)	Dye Absorbance
2.5	0.079
5.0	0.169
10.0	0.369
12.5	0.429
20.0	0.794
40.0	1.445
50.0	1.788
80.0	2.655
100.0	3.308

C. I. REACTIVE BLUE 19

Table A4 Wavelength and dye absorbance at 20 mg/L

Wavelength (nm)	Dye absorbance at 20 mg/L
340	0.257
360	0.195
380	0.169
400	0.110
420	0.057
440	0.039
460	0.049
480	0.077
500	0.124
520	0.187
540	0.274
560	0.353
580	0.437
600	0.444
620	0.418
640	0.353
660	0.180
680	0.056
700	0.015
720	0.003
740	0.004
760	0.001
780	0.001
800	0.000
820	0.000

Table A5 Dye concentration and dye absorbance (600 nm)

Dye Concentration (mg/L)	Dye Absorbance
2.5	0.124
10	0.244
20	0.422
40	0.834
50	1.032
100	2.167

MUIR AND
N ISOTHERM

APPENDIX 4

CALCULATION FOR LANGMUIR AND FREUNDLICH ADSORPTION ISOTHERM

APPENDIX 4: ADSORPTION ISOTHERM

LANGMUIR ADSORPTION ISOTHERM

Table A6 Langmuir calculation for C. I. Reactive Red 180 (Figure 4.9)

Coconut Coir Activated Carbon								
C_o	C_e	$C_o - C_e$	$(C_o - C_e) / C_o$	V	$(C_o - C_e)V$	m	x/m	$C_e / (x/m)$
10	**1.3099**	8.6901	0.8690	0.10	0.8690	1.00	0.8690	**1.5074**
20	**6.2776**	13.7224	0.6861	0.10	1.3722	1.00	1.3722	**4.5747**
30	**12.8319**	17.1681	0.5723	0.10	1.7168	1.00	1.7168	**7.4742**
40	**20.0576**	19.9424	0.4986	0.10	1.9942	1.00	1.9942	**10.0577**
60	**41.3153**	18.6847	0.3114	0.10	1.8685	1.00	1.8685	**22.1118**
70	**50.5173**	19.4827	0.2783	0.10	1.9483	1.00	1.9483	**25.9293**
Charcoal Activated Carbon								
C_o	C_e	$C_o - C_e$	$(C_o - C_e) / C_o$	V	$(C_o - C_e)V$	m	x/m	$C_e / (x/m)$
20	**12.5868**	7.4132	0.3707	0.10	0.7413	1.00	0.7413	**16.9787**
30	**20.4720**	9.5280	0.3176	0.10	0.9528	1.00	0.9528	**21.4861**
40	**27.3957**	12.6043	0.3151	0.10	1.2604	1.00	1.2604	**21.7352**
90	**79.0268**	10.9732	0.1219	0.10	1.0973	1.00	1.0973	**72.0183**
100	**88.7566**	11.2434	0.1124	0.10	1.1243	1.00	1.1243	**78.9408**

Table A7 Langmuir calculation for C. I. Reactive Blue 19 (Figure 4.10)

Coconut Coir Activated Carbon								
C_o	C_e	$C_o - C_e$	$(C_o - C_e) / C_o$	V	$(C_o - C_e)V$	m	x/m	$C_e / (x/m)$
30	**1.5672**	28.4328	0.9478	0.10	2.8433	0.60	4.7388	**0.3307**
40	**3.1026**	36.8974	0.9224	0.10	3.6897	0.60	6.1496	**0.5045**
50	**5.4041**	44.5959	0.8919	0.10	4.4596	0.60	7.4326	**0.7271**
60	**7.7449**	52.2551	0.8709	0.10	5.2255	0.60	8.7092	**0.8893**
70	**11.9789**	58.0211	0.8289	0.10	5.8021	0.60	9.6702	**1.2387**
90	**24.6127**	65.3873	0.7265	0.10	6.5387	0.60	10.8979	**2.2585**
Charcoal Activated Carbon								
C_o	C_e	$C_o - C_e$	$(C_o - C_e) / C_o$	V	$(C_o - C_e)V$	m	x/m	$C_e / (x/m)$
30	**3.5373**	26.4627	0.8821	0.10	2.6463	0.60	4.4104	**0.8020**
50	**7.3778**	42.6222	0.8524	0.10	4.2622	0.60	7.1037	**1.0386**
60	**10.9176**	49.0824	0.8180	0.10	4.9082	0.60	8.1804	**1.3346**
70	**16.3169**	53.6831	0.7669	0.10	5.3683	0.60	8.9472	**1.8237**
80	**22.2765**	57.7235	0.7215	0.10	5.7723	0.60	9.6206	**2.3155**
90	**29.5775**	60.4225	0.6714	0.10	6.0423	0.60	10.0704	**2.9371**

Note:

***C_o** is initial concentration of dye solution, **C_e** is final concentration of dye solution, **V** is volume of dye solution in Liter, **m** is mass of adsorbent in gram and **x** is $(C_o - C_e)V$.*

FREUNDLICH ADSORPTION ISOTHERM

Table A8 Freundlich calculation for C. I. Reactive Red 180 (Figure 4.11)

Coconut Coir Activated Carbon									
C_o	C_e	$C_o - C_e$	$(C_o - C_e) / C_o$	V	$(C_o - C_e)V$	m	x/m	$\text{Log } C_e$	$\text{Log } (x/m)$
10	1.3099	8.6901	0.8690	0.10	0.8690	1.00	0.8690	**0.1172**	**-0.0610**
20	6.2776	13.7224	0.6861	0.10	1.3722	1.00	1.3722	**0.7978**	**0.1374**
60	41.3153	18.6847	0.3114	0.10	1.8685	1.00	1.8685	**1.6161**	**0.2715**
70	50.5173	19.4827	0.2783	0.10	1.9483	1.00	1.9483	**1.7034**	**0.2896**
80	59.4569	20.5431	0.2568	0.10	2.0543	1.00	2.0543	**1.7742**	**0.3127**
Charcoal Activated Carbon									
C_o	C_e	$C_o - C_e$	$(C_o - C_e) / C_o$	V	$(C_o - C_e)V$	m	x/m	$\text{Log } C_e$	$\text{Log } (x/m)$
20	12.5868	7.4132	0.3707	0.10	0.7413	1.00	0.7413	**1.0999**	**-0.1300**
30	20.4720	9.5280	0.3176	0.10	0.9528	1.00	0.9528	**1.3112**	**-0.0210**
40	27.3957	12.6043	0.3151	0.10	1.2604	1.00	1.2604	**1.4377**	**0.1005**
50	36.6474	13.3526	0.2671	0.10	1.3353	1.00	1.3353	**1.5640**	**0.1256**
80	64.7634	15.2366	0.1905	0.10	1.5237	1.00	1.5237	**1.8113**	**0.1829**

Table A9 Freundlich calculation for C. I. Reactive Blue 19 (Figure 4.12)

Coconut Coir Activated Carbon									
C_o	C_e	$C_o - C_e$	$(C_o - C_e) / C_o$	V	$(C_o - C_e)V$	m	x/m	$\log C_e$	$\log (x/m)$
30	1.5672	28.4328	0.9478	0.10	2.8433	0.60	4.7388	**0.1951**	**0.6757**
40	3.1026	36.8974	0.9224	0.10	3.6897	0.60	6.1496	**0.4917**	**0.7888**
50	5.4041	44.5959	0.8919	0.10	4.4596	0.60	7.4326	**0.7327**	**0.8711**
60	7.7449	52.2551	0.8709	0.10	5.2255	0.60	8.7092	**0.8890**	**0.9400**
70	11.9789	58.0211	0.8289	0.10	5.8021	0.60	9.6702	**1.0784**	**0.9854**
100	25.6023	74.3977	0.7440	0.10	7.4398	0.60	12.3996	**1.4083**	**1.0934**
Charcoal Activated Carbon									
C_o	C_e	$C_o - C_e$	$(C_o - C_e) / C_o$	V	$(C_o - C_e)V$	m	x/m	$\log C_e$	$\log (x/m)$
50	7.3778	42.6222	0.8524	0.10	4.2622	0.60	7.1037	**0.8679**	**0.8515**
60	10.9176	49.0824	0.8180	0.10	4.9082	0.60	8.1804	**1.0381**	**0.9128**
70	16.3169	53.6831	0.7669	0.10	5.3683	0.60	8.9472	**1.2126**	**0.9517**
80	22.2765	57.7235	0.7215	0.10	5.7723	0.60	9.6206	**1.3478**	**0.9832**
90	29.5775	60.4225	0.6714	0.10	6.0423	0.60	10.0704	**1.4710**	**1.0030**

Note:

***C_o** is initial concentration of dye solution, **C_e** is final concentration of dye solution, **V** is volume of dye solution in Liter, **m** is mass of adsorbent in gram and **x** is $(C_o - C_e)V$.*